VOL. XIX. MAY, 1897. NO. 5.

AMERICAN CHEMICAL JOURNAL.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON URETHANES.

BY OTTO FOLIN.

Sodium methylate and acetbromamide in methyl alcohol solution do not yield a hydroxylamine derivative according to the following equation:

$$CH_3CONHBr + NaOCH_3 = CH_3CONHOCH_3 + NaBr;$$

but a molecular rearrangement, analogous to that observed by Hofmann[1] in the action of alkalies on acid bromamides, occurs in the course of the reaction, and a urethane is obtained in place of the isomeric hydroxylamine ether:[2]

$$CH_3CONHBr + NaOCH_3 = CH_3NHCOOCH_3 + NaBr.$$

A similar rearrangement occurs in the action of sodium methylate on paranitrobenzbromamide and on succinimide bromide.[3]

The investigations described in this paper were undertaken at the suggestion of Dr. Stieglitz and Dr. Lengfeld for the purpose of determining whether the reaction

$$RCONHBr + NaOCH_3 = RNHCOOCH_3 + NaBr$$

is general, or if it is possible to prevent the rearrangement and effect direct substitution by varying the positive and negative character of the group R.

[1] Hofmann: Ber. d. chem. Ges., 14, 2725; 15, 408, etc.
[2] Lengfeld and Stieglitz: This JOURNAL, 16, 370; Stieglitz: *Ibid*, 18, 752.
[3] This JOURNAL, 15, 215, 504.

In the course of their investigations on urethanes, Lengfeld and Stieglitz[1] obtained chlorformanilide by the action of phosphorus pentachloride on phenylurethane :

$$C_6H_5HNCOOC_2H_5 + PCl_5 = C_6H_5NH.COCl + C_2H_5Cl + POCl_3.$$

The action of phosphorus pentachloride on substituted urethanes, as well as the action of phosphorus pentachloride and of phosgene on urethane itself was therefore made a part of this investigation in order to test the applicability of the reaction.

I. PREPARATION OF URETHANES FROM ACID BROMAMIDES.

Action of Sodium Methylate on Benzbromamide.

To the cool solution of 1.72 grams sodium in 68 grams pure anhydrous methyl alcohol was added 15 grams benzbromamide.[2] The bromide dissolved readily, but no reaction occurred in the cold. The solution was boiled on the water-bath for an hour, when a test with potassium iodide and hydrochloric acid showed that no unchanged bromamide remained. After distilling off the greater part of the alcohol, the residue was allowed to evaporate to dryness at ordinary temperatures, and the resulting product extracted with ether.

The ether extract was distilled under reduced pressure and finally recrystallized from hot water. Perfectly white crystals, melting sharply at 47°, were obtained. The compound has the composition and all the properties of methyl phenylcarbamate, $C_6H_5NHCOOCH_3$, (melting-point 47°). A synthetic preparation of the substance was identical with it in every respect; a mixture of the two melted sharply at 47°.

0.1354 gram substance gave 11.65 cc. moist nitrogen at 747 mm. and 24°.

	Calculated for $C_8H_9NO_2$.	Found.
N	9.27	9.53

The main product of the reaction is therefore methyl-phenylcarbamate. Methyl benzhydroxamate, $C_6H_5CONHOCH_3$, might, however, have been formed by direct substitution to a

[1] This JOURNAL, **16**, 70.

[2] Hoogewerff and Van Dorp: Rec. d. Trav. chim. d. Pays. Bas., **8**, 188.

very slight extent as a by-product. As this substance is somewhat soluble in water, and easily soluble in ether, advantage was taken of these properties to determine whether it is formed at all by the action of sodium methylate on benzbromamide. 50 grams of the bromamide was treated as described above with the calculated amount of sodium methylate. The hard, dry mass that remained after removing the alcohol in neutral solution in a vacuum was broken up with the aid of a few drops of ether, and then extracted with water. The extract was repeatedly shaken out with ether; the ethereal solutions dried over potassium carbonate, and the ether distilled off. A small quantity of pure methyl phenylcarbamate remained; hence no methylbenzhydroxamate was formed even as a by-product. No direct replacement of the bromine atom takes place; rearrangement and formation of urethane occur quantitatively according to:

$$C_6H_5CONHBr + NaOCH_3 = C_6H_5NHCOOCH_3 + NaBr.$$

Action of Sodium Methylate on Metanitrobenzbromamide.

Metanitrobenzbromamide was prepared as described by Hoogewerff and Van Dorf.[1] The substance when precipitated by addition of acetic acid to the alkaline solution came down in a very sticky paste. It could be washed only by taking a very small portion at a time, and it was dried on clay plates and in vacuum desiccators over sulphuric acid for seven days before it was perfectly dry.

Methyl m-Nitrophenylcarbamate, $m.NO_2C_6H_4NHCOOCH_3$. —Two grams sodium (1 atom), dissolved in 80 grams pure methyl alcohol, was heated on the water-bath with 2.15 grams *m*-nitrobenzbromamide (1 molecule) for one hour. A yellow crust formed on the sides of the flask during the heating and, on cooling, a large quantity of a yellow crystalline precipitate was formed. The substance was identified as *m*-nitrophenylmethylurethane. After removing the precipitate by filtration most of the alcohol was distilled off. The mixture changes in color and decomposes on prolonged heating, and the evaporation was, therefore, completed at ordinary temperatures. The residue was extracted with chloroform, and the extract

[1] Rec. trav. chim., 8, 193.

gave by recrystallization from warm chloroform well-formed octahedrons, melting at 147°–149°. The compound is *methyl metanitrophenylcarbamate*, *m*-$NO_2C_6H_4NHCOOCH_3$, and is obtained in quantities corresponding to 90 per cent. of the theoretical.

0.1153 gram substance gave 15.2 cc. moist nitrogen (over 30 per cent. caustic potash) at 743 mm. and at 22°.

	Calculated for $C_8H_8N_2O_4$.	Found.
N	14.28	14.66

Methyl metanitrophenylcarbamate, not being known, was prepared synthetically from *m*-nitraniline and methyl chlorformate. It was identical with the body just described.

Action of Sodium Methylate on Orthonitrobenzbromamide.

o-Nitrobenzbromamide has also been prepared by Hoogewerff and Van Dorp.[1] The compound is not so pasty as the meta derivative aud can be washed and dried very rapidly.

Methyl-o-Nitrophenylcarbamate, *o*-$NO_2C_6H_4NHCOOCH_3$.—10.5 grams *o*-nitrobenzbromamide was added to 1 gram of sodium dissolved in 40 grams methyl alcohol. It dissolved, but no noticeable reaction took place in the cold. The mixture was then heated on the water-bath for twenty minutes. At the end of this time there was no unchanged bromamide left in the solution. The slightly alkaline solution was then acidified with a few drops of dilute acetic acid, and the alcohol allowed to evaporate at ordinary temperatures. The residue, extracted ten times with boiling (40°–50°) ligroïn, gave about 7 grams of a dark yellow oil which, on cooling, solidified. This substance is methyl *o*-nitrophenylcarbamate, mixed with a small quantity of *o*-nitraniline. To remove the latter the mixture was dissolved in pure, cold chloroform and *o*-nitraniline hydrochloride precipitated by means of dry hydrochloric acid gas. The urethane was then precipitated with ligroïn and, after repeated recrystallization from ligroïn, its melting-point was found constant at 53°. *o*-Nitrophenylurethane consists of well-formed greenish-yellow crystals, and is quite soluble in all the ordinary organic solvents except low-boiling ligroïn.

[1] Rec. trav. chim., 8, 191.

0.2977 gram substance gave 0.5383 gram CO_2 and 0.1192 gram H_2O.

	Calculated for $C_8H_8N_2O_4$.	Found.
C	48.98	49.31
H	4.08	4.45

In order to obtain the yield of urethane indicated above (90 per cent.) it is essential that the experiment should be performed as described. As soon as heat is applied to the alcoholic solution of sodium methylate and *o*-nitrobenzbromamide, it turns red and the color deepens as the heating is continued, until at the end of about one hour it is found that the chief product is *o*-nitraniline, most of the urethane evidently being saponified.

As methyl *o*-nitrophenylcarbamate is comparatively unstable at higher temperatures, I attempted to complete the reaction at a temperature below that of boiling methyl alcohol. At 50° I found that the reaction goes about the same as at 66°–70°, and the relative amount of each of the various products obtained varies with the time the heating is continued. At 30°, on the other hand, the result is somewhat different. The reaction proceeded very slowly and was not completed at the end of the fifth hour. The solution remained clear at first, but after a couple of hours, a precipitate, consisting of small white crystals, appeared. This increased constantly in amount until it was removed by filtration at the end of five hours, after which the reaction was completed by boiling on the water-bath for fifteen minutes. The precipitate melted at 220°. It is insoluble in all the ordinary organic solvents except acetone. The same compound was obtained in larger quantities by Swartz,[1] who also made a closer investigation of it, and by analysis and synthesis showed it to be *o*-nitrophenyl-*o*-nitrobenzoylurea,

$$(o)\text{-}NO_2C_6H_4NHCONHCOC_6H_4NO_2\text{-}(o).$$

The substance obtained in this reaction is in every respect identical with the synthetic product prepared by Swartz. Its formation here is due to the reducing action of methyl alcohol on a part of the *o*-nitrobenzbromamide, giving formaldehyde and

[1] See This JOURNAL, 19, 295.

o-nitrobenzamide, the latter of which is then acted upon by a molecule of *o*-nitrophenyl isocyanate, formed by the rearrangement of a second molecule of *o*-nitrobenzbromamide.[1] The odor of the aldehyde was quite distinct.

1. $NO_2C_6H_4CONHBr + NaOCH_3 = NO_2C_6H_4CONH_2 + CH_2O + NaBr.$

2. $NO_2C_6H_4CONHBr + NaOCH_3 = NO_2C_6H_4N{=}CO + NaBr + HOCH_3.$

3. $NO_2C_6H_4N = CO + NH_2COC_6H_4NO_2 = NO_2C_6H_4NHCONHCOC_6H_4NO_2.$

Action of Sodium Methylate on Metabrombenzbromamide.

Pure *m*-brombenzoic acid was converted successively with phosphorus pentachloride and ammonia into the acid chloride and *m*-brombenzamide. The latter crude product was not perfectly white, but it was quite pure and had a melting-point somewhat higher than that found by Engler,[2] 150°. Recrystallized from chloroform, it was obtained in perfectly white crystals, melting at 153°–4°. Analysis showed its purity:

0.2014 gram substance gave 12.6 cc. moist nitrogen at 740.3 mm. and 21°.

	Calculated for C_7H_4NOBr.	Found.
N	7.00	6.97

Metabrombenzbromamide, *m*-$BrC_6H_4CONHBr$.—This bromide was not known; but it was prepared from the amide by exactly the same method as that used by Hoogewerff and Van Dorp in the preparation of the nitrobenzbromamides. The yield was good. The compound was slightly colored and consisted of prismatic, microscopic needles, melting at 105°. The bromine attached to the nitrogen was determined in the crude product, and no attempt was made to obtain it in perfectly pure condition:

	Calculated for $(C_7H_4BrON)Br$.	Found.
Active bromine	28.7	27.9

[1] Hofmann: Ber. d. chem. Ges., **14**, 2725; Lengfeld and Stieglitz: This JOURNAL, **15**, 506; Stieglitz: *Ibid*, **18**, 752.

[2] Ber. d. chem. Ges., **4**, 708.

Methyl Metabromphenylcarbamate, *m*-$BrC_6H_4NHCOOCH_3$. —Five grams *m*-brombenzbromamide was added to 0.4 gram sodium dissolved in 20 grams absolute methyl alcohol, and the mixture heated for one hour. The solution was neutralized and the greater part of the alcohol distilled off. On adding water to the remainder, a white precipitate came down. This was recrystallized from chloroform by the addition of ligroïn and analyzed.

0.2678 gram substance gave 15.25 cc. moist nitrogen at 749.3 mm. and 25°.

	Calculated for $C_8H_8NO_2Br$.	Found.
N	6.09	6.29

Methyl *m*-bromphenylcarbamate is a white crystalline compound melting at 84.5°–85.5°; insoluble in water and soluble in all the ordinary organic solvents except ligroïn. The yield of urethane in the above reaction is from 80 to 90 per cent. of the theoretical, and the remainder of the bromamide is reduced to the amide and is recovered.

As the work just described shows that the rearrangement of the acid bromamides, RCONHBr, occurs almost quantitatively, even when R is strongly negative ($R = C_6H_5$; *o*-$NO_2C_6H_4$; *m*-$NO_2C_6H_4$; *m*-BrC_6H_4), the effect of positive radicals was studied. A dialkylamidobenzamide, $R_2NC_6H_4CONH_2$, was first chosen rather than an amidobenzamide in order to remove the possibility of the hypobromite acting on the amide group attached to the benzene ring, in preparing the bromamide. As no such amides had been prepared and described, a few experiments were first made to determine the best method for obtaining them.

p-Diethylamidobenzamide, *p*-$(C_2H_5)_2NC_6H_4CONH_2$.—Michler obtained dimethylamidobenzoic acid by heating dimethylaniline and phosgene in sealed tubes to 50° and pouring the resulting mixture into water.[1] To prepare the amide 62 grams phosgene was passed into 95 grams diethylaniline in a flask attached to an inverted condenser cooled with a freezing-mixture. The two reacted slowly, the mixture gradually solidifying to a white mass, which was colored first red and later a deep blue:

[1] Ber. d. chem. Ges., 9, 400, etc.

$$(C_2H_5)_2NC_6H_4 + COCl_2 = (C_2H_5)_2NC_6H_4COCl + HCl.$$

The crude chloride thus formed was slowly added to an excess of strong, cold ammonia. The reaction was quite violent; but only 12 grams of the expected acid amide was obtained, the greater portion of the acid chloride being converted into diethylamidobenzoic acid instead. The amide obtained in this reaction is not pure. It is mixed with benzophenone derivatives, and a blue coloring matter, which can be removed only very slowly and with great loss by fractional precipitation from hot alcohol.

Since diethylamidobenzoic acid is easily purified, it was thought best first to prepare this pure, and then convert it by means of phosphorus pentachloride and ammonia into the amide. The acid was prepared by Michler's method and purified by dissolving in alkalies and reprecipitating the acid with acetic acid (melting-point 188°).

Action of Phosphorus Pentachloride on p-Diethylamidobenzoic Acid.—Phosphorus pentachloride and diethylamidobenzoic acid were mixed in molecular quantities. Action set in only with great difficulty at 60°–70°, and the mass became very brown as the reaction proceeded. The amide obtained by the action of ammonia on this product was quite impure. A very smooth reaction can be brought about by first passing dry hydrochloric acid into a chloroform solution of diethylamidobenzoic acid, thus converting it into the hydrochloride, $HCl(C_2H_5)_2NC_6H_4COOH$, before adding phosphorus pentachloride. Reaction with the latter now sets in at once at 40°–50°, a clear, colorless mixture of phosphorus oxychloride and the hydrochloride of diethylamidobenzoic acid chloride being obtained. This behavior of diethylamidobenzoic acid toward phosphorus pentachloride is further evidence that it is really a salt, perhaps $HN(C_2H_5)_2C_6H_4COO$, which like other salts, would not react so readily with phosphorus pentachloride. The hydrochloride, $ClHN(C_2H_5)_2C_6H_4COOH$, is a true acid and reacts as smoothly with phosphorus pentachloride as any other acid:

$$\begin{matrix} H \\ Cl \end{matrix}\!\!>\!N(C_2H_5)_2C_6H_4COOH + PCl_5 = \begin{matrix} H \\ Cl \end{matrix}\!\!>\!N(C_2H_5)_2C_6H_4COCl + HCl + POCl_3.$$

The acid chloride thus obtained gives, with ammonia, diethylamidobenzamide in very pure condition, with a yield of 50 per cent. Considerable quantities of regenerated acid were always recovered from the ammoniacal filtrate, with only slight loss of material.

p-Diethylamidobenzamide is a white crystalline solid melting at 136°–137°. It is readily soluble in hot water and in hot alcohol, but is very little soluble in any of the other organic solvents.

0.1878 gram substance gave 24.2 cc. moist nitrogen at 740 mm. and 17°.

	Calculated for $C_{11}H_{16}N_2O$.	Found.
N	14.58	14.61

Ethyl Diethylamidobenzoate, $(C_2H_5)_2NC_6H_4COOC_2H_5$. — In place of converting diethylamidobenzoic acid into the amide by means of its chloride, an attempt was made to prepare it from its ester. The best yield of ethyl diethylamidobenzoate (75 per cent.) was obtained by dissolving the acid in alcohol and heating it with from 4 to 5 equivalents of sulphuric acid on the water-bath for ten hours. Ethyl diethylamidobenzoate is described by Michael and Wing as an oil which solidifies in a freezing-mixture, but melts again at ordinary temperatures.[1] I found it to be a white solid consisting of irregular rhombohedral plates, insoluble in water and very soluble in ether and chloroform. It was repeatedly recrystallized from hot alcohol until it melted sharply at 43°.

0.2942 gram substance gave 0.7616 gram CO_2 and 0.2464 gram H_2O.

	Calculated for $C_{13}H_{19}NO_2$.	Found.
C	70.60	70.59
H	8.6	9.31

Ethyl Diethylamidobenzoate and Ammonia.—From the ester thus prepared I was unable to get the corresponding amide by treatment with ammonia. The ethyl diethylamidobenzo-

[1] This JOURNAL, 7, 197.

ate was heated with a large excess of aqueous ammonia and with alcoholic ammonia on the water-bath; it was left in glass-stoppered bottles with concentrated aqueous ammonia and with saturated alcoholic ammonia for several weeks, but not a trace of the acid amide was obtained. The ester remained unchanged.

The yield of diethylamidobenzamide obtained from diethylaniline by way of diethylamidobenzoic acid being rather unsatisfactory, a better yield of such an amide was sought by converting dimethylaniline into an amide by means of the nitrile, $(CH_3)_2NC_6H_4CN$.

Action of Cyanogen Bromide on Dimethylaniline.—As the hydrogen atom in the para position to the amide group in dimethylaniline is very easily replaced, the latter might, it seemed, be converted by the action of cyanogen bromide into dimethylamidobenzonitrile. Dimethylaniline in dry chloroform solution was first converted into its hydrochloride and mixed with one molecule of cyanogen bromide. Aluminium chloride was then added, a small portion at a time; it produced a lively reaction in the mixture. All but the aluminium chloride went into solution. The latter was removed by filtration; the filtrate distilled, and the solid residue distilled with steam. A crystalline solid came over, which was soluble in all the organic solvents and melted at 55°–56°. The melting-point and all the properties of the compound correspond to those of parabromdimethylaniline. It was prepared synthetically and the two were identical.

The reaction, therefore, did not take place as was expected and the bromine, instead of the cyanogen radical, was found to have replaced the para hydrogen atom in dimethylaniline.

$$(CH_3)_2NC_6H_4H + BrCN = (CH_3)_2NC_6H_4Br + HCN.$$

Action of Cyanogen Bromide on Parabromdimethylaniline.—Cyanogen bromide failing to give the nitrile by acting on dimethylaniline, its action on *p*-bromdimethylaniline in the presence of sodium was tried, in the attempt to fulfil the equation:[1]

$$(CH_3)_2NC_6H_4Br + 2Na + BrCN = (CH_3)_2NC_6H_4CN + 2NaBr.$$

[1] Claus: Ber. d. chem. Ges., **16**, 915.

2.75 grams sodium wire in 100 grams absolute ether was cooled in a freezing-mixture. 12 grams *p*-bromdimethylaniline[1] and 6.26 grams cyanogen bromide were mixed and added to the sodium in the ether.

Both bodies dissolved in the ether, but no reaction took place until the flask was taken out of the freezing-mixture. The reaction was very rapid, as the contents of the flask began to get a little warmer, but was easily regulated by cooling. After the reaction was completed, a solid containing only sodium bromide and sodium cyanide was removed by filtration and the ether distilled off. The remaining residue was found to be only unchanged *p*-bromdimethylaniline. The cyanogen bromide, therefore, is decomposed by the sodium and no nitrile is obtained.

p-Dimethylamidobenzonitril, *p*-$(CH_3)_2NC_6H_4CN$.—By treating the diazochloride of *p*-amidodimethylaniline with Sandmeyer's potassium cyanide-copper sulphate solution, Ahrens[2] obtained an oil from which he was unable to isolate the nitrile, but which gave dimethylamidobenzoic acid with alcoholic potash, proving the presence of the nitrile. No statement of the yield being made, Ahrens' work was repeated by me.

The oil described by him was obtained, and was distilled with steam. At first a colorless oil came over which was found to be dimethylaniline. Afterwards a light-colored substance was carried over, which solidified in the condenser. It was purified by precipitating it from ether solution with ligroïn, and thus obtained in slightly yellowish needles, which melted at 74°–76°. It is very soluble in chloroform and ether, and very little soluble in low-boiling ligroïn. By prolonged boiling with strong alcoholic potash it is converted into *p*-dimethylamidobenzoic acid (melting-point 235°). Its properties show it to be *p*-dimethylamidobenzonitrile, but the yield was too small to make its preparation an advantageous one for the purpose of obtaining a dialkylamidobenzamide. These are therefore best prepared from the dialkylamidobenzoic acids by the successive action of hydrochloric acid, phosphorus pentachloride, and ammonia, as described above.

[1] Weber: Ber. d. chem. Ges., 8, 715; 10, 763. [2] Ber. d. chem. Ges., 20, 2958.

Action of Potassium Hypobromite on p-Diethylamidobenzamide.—One gram diethylamidobenzamide was added to a cold solution containing the calculated quantity of potassium hypobromite. A part of the amide dissolved, and a precipitate was formed which quickly changed to a dark-brown color. The solution was filtered and cold boric acid added to the filtrate. A brown sticky precipitate resembling the first one was thrown down. It dissolved in hydrochloric acid and was again precipitated with ammonia; but it did not give off bromine with the acid or nitrogen with ammonia. The dry substance gave a very distinct dark green flame when ignited with copper oxide, and was probably some compound containing one or more bromine atoms in the benzene ring. It certainly was not diethylamidobenzbromamide, $(C_2H_5)_2NC_6H_4CONHBr$. As acid chloramides are rather more stable than the corresponding bromamides, diethylamidobenzamide was allowed to react with molecular quantities and with excess of hypochlorous acid. A yellow, sticky precipitate was extracted with ether, and a substance obtained which gave the test for halogen amide with potassium iodide and hydrochloric acid when freshly prepared; but it rapidly decomposed, and when left over night it no longer gave the test for halogen amide. On account of this instability of the halogen amides, $R_2NC_6H_4CONHX$, the action of sodium methylate on them could not be investigated.

Action of Hypobromite on Metamidobenzamide. — Another attempt was made with metamidobenzamide. This amide was treated with cold potassium hypobromite solution in the usual manner. A reddish precipitate was obtained which, when placed on clay plates, soon turned to a black amorphous mass, containing bromine and not melting below 280°. The experiment was repeated in various ways, but with no better results. The black amorphous mass was extracted with ether, alcohol and chlorform in a Soxhlet apparatus; but each extract was amorphous, and no definite product was isolated. Several of these extracts, as well as the residue, were heated in sealed tubes with hydrochloric acid and the products examined for metaphenylenediamine, but none was found.

Having thus failed to obtain an acid bromamide containing the amido or dialkylamido groups in the benzene ring, probably on account of the remarkable reactivity which such positive groups give to the benzene ring, I succeeded in preparing an analogous acid bromamide in the aliphatic series, on which the action of sodium methylate was tried. Carbomethoxy-β-amidopropionamide, $CH_3O_2CNHCH_2CH_2CONH_2$, was selected because it can be prepared without much difficulty.[1]

Carbomethoxy-β-amidopropionbromamide, $CH_3O_2CNHCH_2CH_2CONHBr$.—Two grams caustic potash was dissolved in a very small quantitity of water, and 2.1 grams bromide added at —5°, and to this cold solution was added 2 grams carbomethoxy-β-amidopropionamide. The latter dissolved in a few minutes. Cold acetic acid was next added in slight excess without letting the temperature of the mixture rise above —5°. The acetic acid does not precipitate the bromamide at once, as it does in the precipitation of the aromatic ones; but in a few minutes the precipitate begins to form and then comes down very rapidly. The yellow crystalline bromamide was rapidly filtered and washed with a small quantity of cold water. It is easily soluble in water and no attempt was made to obtain it in perfectly pure condition. By using very small quantities of cold water a good yield of bromamide (80 per cent. pure) was obtained. Crude carbomethoxy-β-amidopropionbromamide is a white crystalline compound and melts with decomposition at 117°–118°.

Action of Sodium Methylate on Carbomethoxy-β-amidopropionbromamide.

0.4 gram sodium was dissolved in 20 grams absolute methyl alcohol and 4.5 grams carbomethoxy-β-amidopropionbromamide added. The latter dissolved and the mixture was boiled half an hour, when no bromamide was left unchanged. The solution was carefully neutralized with acetic acid and the mixture allowed to evaporate to dryness in a vacuum-desiccator. The white solid mass that remained was extracted with chloroform, and the chloroform solution washed

[1] Lengfeld and Stieglitz: This JOURNAL, 15, 512.

with small quantities of dilute hydrochloric acid, caustic soda solution and water. The solution was then dried over calcium chloride, and the chloroform distilled. An oil remained which solidified as soon as it began to cool. The weight of this solid was only 0.3 gram. Some was undoubtedly removed by the repeated washings of the chloroform solution; but the main object sought was purity of substance rather than a larger yield. It was recrystallized from dilute alcohol and from water, giving 0.2 gram of a compound melting at 132°–3°. The melting-point, crystalline form and solubilities of this compound are the same as those ascribed by Franchimont and Klobbie[1] to the dimethyl ester of ethylenedicarbamic acid, $CH_3O_2CNHCH_2CH_2NHCO_2CH_3$.

0.1484 gram substance gave 22 cc. moist nitrogen at 744 mm. at 24°.

	Calculated for $C_6H_{12}N_2O_4$.	Found.
N	15.91	16.35

The usual rearrangement,

$$CH_3O_2CNHCH_2CH_2CONHBr + NaOCH_3 = CH_3O_2CNHCH_2CH_2NHCO_2CH_3 + NaBr,$$

occurs, therefore, in this case; but exactly what yield of urethane can be obtained, or what other products are formed, was not investigated on account of the small amount of material on hand.

The above experiments show that the reaction,

$$RCONHBr + NaOCH_3 = RNHCOOCH_3 + NaBr,$$

is quite general, as it succeeded with all acid bromamides that could be isolated and investigated.

II. ACTION OF PHOSPHORUS PENTACHLORIDE ON URETHANES.

Action of Phosphorus Pentachloride on Phenylurethane.

Lengfeld and Stieglitz[2] obtained, by the action of phosphorus pentachloride on 10 grams phenylurethane, about 3 grams chlorformanilide,

$$C_6H_5NHCOOC_2H_5 + PCl_5 = C_6H_5NHCOCl + C_2H_5Cl + POCl_3.$$

The chief reason why a larger yield was not obtained

[1] Rec. d. trav. chim. Phys. Bas., 7, 258. [2] This JOURNAL, 15, 71.

seems to be that a part of the chlorformanilide at the temperature of the reaction (50°–60°) lost hydrochloric acid giving phenyl isocyanate, which is quite soluble in ligroïn.[1] The reaction of phosphorus pentachloride and phenylurethane was repeated under somewhat different conditions to improve the yield.

6.25 grams phosphorus pentachloride and 5 grams urethane gave 1.5 grams chlorformanilide after removing the phosphorus oxychloride with ligroïn (boiling-point 40°–60°). The mixed liquids were transferred from the solid precipitate into another flask and dry hydrochloric acid was then passed through the mixture. In a few minutes crystals began to appear. The current of hydrochloric acid was continued for about half an hour, the ligroïn being renewed from time to time. 0.8 gram chlorformanilide was thus obtained, increasing the yield, therefore, over fifty per cent. The best conditions for preparing chlorformanilide were found to be as follows:

10 grams urethane was acted upon by 12.5 grams phosphorus pentachloride. Pure, dry chloroform was then added in small quantity, and hydrochloric acid gas passed through the solution at ordinary temperatures until nearly all the phosphorus oxychloride had been driven off, the chloroform being renewed as fast as it was removed. The dissociation into the volatile isocyanate and hydrochloric acid is diminished by the stream of hydrochloric acid gas, and chlorformanilide, not being volatile at ordinary temperatures, remains. The latter was then precipitated as before by the addition of low-boiling ligroïn and nearly 6 grams, or about 60 per cent. of the theoretical yield, was obtained, which is almost twice as much as was obtained without the addition of dry hydrochloric acid.

Action of Phosphorus Pentachloride on Metanitrophenylurethane.

8.5 grams *m*-nitrophenylurethane and 8.5 grams phosphorus pentachloride were heated together in a dry flask to 55°–65°. No reaction took place until some of the urethane was brought into solution by the addition of a little dry chloroform. The

[1] Werner: Ber. d. chem. Ges., **26**, 1565; Hentchel: *Ibid*, **18**, 1178.

reaction-product was cooled in a freezing-mixture and dry hydrochloric acid passed through. In a few minutes a white crystalline solid appeared, and increased rapidly until the whole of the contents in the flask solidified. More chloroform was added, and was driven off by a continuous, strong stream of hydrochloric acid, in order to carry off most of the phosphorus oxychloride. Cold ligroïn was added and the precipitate rapidly filtered and washed. 6.6 grams *m*-nitrophenylurea chloride or 81 per cent. of the theoretical yield was obtained. Chlorformmetanitranilide is a nearly colorless crystalline solid, which melts at 102° with decomposition.

I. 0.2956 gram substance gave 0.04895 gram chlorine.

II. 0.2877 gram substance gave 0.04772 gram chlorine (Volhard).

	Calculated for $C_7H_5N_3O_3Cl$.	Found. I.	II.
Cl	17.72	16.56	16.59

Urea chlorides decompose readily, losing hydrochloric acid, and hence the figures are low.

Metanitrophenylurea, *m*-$NO_2C_6H_4NHCONH_2$. — In order more fully to identify the urea chloride obtained in the last experiment, a small amount of it was added to ammonia. It reacted violently, and a yellow crystalline solid was formed, which after recrystallization from hot water, melted at 195°, with slight decomposition. Hofmann[1] describes *m*-nitrophenylurea as consisting of long yellow needles. If the hot water solution is allowed to cool very slowly the substance does come down as described by Hofmann; but if rapidly cooled, it comes down in plates.

0.1788 gram substance gave 36 cc. moist nitrogen at 746 mm. and 19°.

	Calculated for $C_7H_7N_3O_3$.	Found.
N	23.20	23.06

Metanitrophenyl Isocyanate, *m*-$NO_2C_6H_4NCO$.—Metanitrophenylurea chloride was heated in a current of dry air to 110°–140° until no trace of hydrochloric acid could be detected in the air that had passed through the apparatus. The residue

[1] Ann. Chem. (Liebig), **67**, 156; **70**. 137.

was then extracted with sodium-dried ligroïn. The isocyanate is quite soluble in boiling ligroïn, and on cooling it comes down as a microcrystalline, inodorous, white solid, melting at 49°–50°.

0.1957 gram substance gave 30.9 cc. moist nitrogen at 741 mm. and 23°.

	Calculated for $C_7H_4N_2O_4$.	Found.
N	17.08	17.33

Metanitrophenyl isocyanate has all the characteristics of phenyl isocyanate, except the odor, and readily gives the usual isocyanate addition-products. Methylnitrophenylurethane, *m*-$NO_2C_6H_4NHCOOCH_3$, (melting-point 148°) was obtained by the action of isocyanate on absolute methyl alcohol. The corresponding ethylurethane[1] (melting-point 63°) was similarly obtained from ethyl alcohol. With ammonia the reaction is very violent, giving the *m*-nitromonophenylurea just described above.

Metanitrophenyl-m-nitrobenzoylurea, *m*-$NO_2C_6H_4NHCONHCOC_6H_4NO_2$-*m*.—Molecular quantities of metanitrophenyl isocyanate and *m*-nitrobenzamide were heated to 150°. The melted mixture soon solidified and the product was found to be *m*-nitrophenyl-*m*-nitrobenzoylurea, melting at 230°.

$$m\text{-}NO_2C_6H_4NCO + H_2NOCC_6H_4NO_2\text{-}m = NO_2C_6H_4NHCONHCOC_6H_4NO_2\text{-}m.$$

This urea is isomeric with the corresponding ortho derivative obtained by me as a by-product in the action of sodium methylate on orthonitrobenzbromamide.

0.1577 gram substance gave 24.9 cc. moist nitrogen at 740 mm. and 24°.

	Calculated for $C_{14}H_{10}N_4O_6$.	Found.
N	16.97	17.32

Action of Phosphorus Pentachloride on Metabromphenylurethane.

Metabromphenylurethane reacted with phosphorus pentachloride quite as readily as did the *m*-nitrophenylurethane and a good yield of white, crystalline *m*-bromphenylurea chloride, *m*-$BrC_6H_4NHCOCl$, was obtained.

[1] Struve und Radenhausen: J. prakt. Chem., **52**, 230. They give the melting-point 56°. Swartz: This JOURNAL, **19**, 295, found the melting-point 65°.

The compound was identified by treating it with strong ammonia thus producing

Metabromphenylurea, *m*- $BrC_6H_4NHCONH_2$. — *m*-Bromphenylurea is very little soluble in all the ordinary organic solvents except alcohol. It was purified by dissolving an absolute alcohol and precipitating with ether and ligroïn. White needles, softening at 162°, melting at 164°–5°.

0.1514 gram substance gave 18.15 cc. moist nitrogen at 742 mm. and 25.3°.

	Calculated for $C_7H_7N_2OBr$.	Found.
N	13.02	13.12

These experiments show that with urethanes of the aromatic amines the reaction,

$$RNHCOOCH_3 + PCl_5 = RNHCOCl + CH_3Cl + POCl_3,$$

is general. Methyl chloride is first split off, giving chlorformanilides which are easily isolated, and from which the isocyanates can readily be obtained by the further loss of hydrochloric acid.

Phenyl isocyanate and chlorformanilide, hitherto prepared from aniline and phosgene, can be more conveniently prepared, especially in moderate quantities, by the method just described.[1] And since metanitrobenzoic acid is easily available, and can be readily converted into methyl *m*-nitrophenylcarbamate and its chloride, the latter may often be conveniently used in place of phenyl isocyanate, the melting-points of its derivatives being 15° to 100° higher.

Whether the above reaction is also applicable to the urethanes of the aliphatic amines and to urethane itself remained to be ascertained. I have studied the action of phosphorus pentachloride on urethane.

Preparation of Urethane.

Liebig and Wöhler[2] passed isocyanic vapors into a mixture

[1] In making the urethanes it is not necessary to isolate the bromamides. As has been found by Miss Jeffreys, working under the direction of Dr. Stieglitz, a mixture of the acid amide and bromine dissolved in methyl alcohol may be treated with the solution of sodium methylate, or bromine may be added to such a solution of the amide and the methylate. In this way the urethanes can be prepared from many acid amides in good yield in one to two hours. Miss Jeffreys will report later on this reaction in this JOURNAL. [2] Ann. Chem. (Liebig), **54**, 370; **58**, 260.

of alcohol and ether and obtained in addition to allophanic ethylester small quantities of urethane. The use of potassium isocyanate and hydrochloric acid in place of the isocyanic acid vapors for the preparation of urethane seems never to have been tried. Amato[1] obtained allophanic ether from such a mixture of potassium isocyanate, alcohol, and dilute hydrochloric acid by boiling two days.

A good yield of urethane can nevertheless be obtained from just such a mixture by proceeding as follows: 5 grams potassium isocyanate was dissolved in just enough dilute (50 per cent.) warm alcohol to make a clear solution. This was then slowly added to a strong alcoholic solution of hydrochloric acid containing an excess of acid. The reaction is completed only very slowly on account of the insolubility of potassium isocyanate in alcohol, and the mixture was left standing at ordinary temperatures till the following day. A white precipitate was formed when the two solutions were mixed, and after twenty-four hours it gave off no gas when treated with aqueous hydrochloric acid. The excess of hydrochloric acid was neutralized with barium carbonate, the mixture filtered, and most of the alcohol removed by distillation. The remainder was allowed to evaporate to dryness in a vacuum-desiccator. The residue, extracted with ether, gave, after drying and distilling off the ether, 3.3 grams urethane, corresponding to a yield of 60 per cent. Urethane is quite volatile, and it was found by experiment that a considerable quantity is carried over by the alcohol when the latter is removed by distillation. Such losses could undoubtedly be avoided, and the above yield largely increased by using a Hempel tube in distilling off the alcohol.

Action of Phosphorus Pentachloride on Urethane.

10 grams (1 molecule) urethane and 23.3 grams phosphorus pentachloride (1 molecule) were mixed and at once began to react with evolution of a considerable amount of gas and with the absorption of so much heat that the flask containing the mixture became quite cold. In twenty minutes the reaction seemed to be complete, leaving a clear, colorless liquid in the

[1] Jsb. d. Chem., *1873*, 749.

flask. Gattermann,[1] who prepared carbamic acid chloride, NH_2COCl, by the action of phosgene on ammonium chloride describes it as a white, crystalline body, insoluble in ligroïn, melting at 50° and boiling at 61°–62°. Dry ligroïn produced, however, no precipitate in the above liquid, even when cooled in a freezing-mixture. The ligroïn solution was slowly added to cold aniline, and the resulting white, solid mixture carefully examined for monophenylurea, but none was found.

The gas given off in the cold consists chiefly of hydrogen chloride but, on heating, much ethyl chloride escapes. The reaction was repeated in a current of dry hydrogen chloride, and the mixture distilled at 40 mm. in a current of hydrogen chloride, which was intended to decrease possible loss of chlorformamide by dissociation.[2] The distillate was collected in several different fractions, each of which reacted violently with water, giving carbon dioxide in quantities of only 44 to 66 per cent. of the theoretical for chlorformamide. With aniline no phenylurea could be obtained, with methyl alcohol no methylurethane, all of which experiments show that by the action of phosphorus pentachloride on urethane, unlike that on phenylurethane, no chlorformamide is formed. A final effort to show its presence was based on the fact that chlorformamide very readily gives with urethane ethyl allophanate,[3] which is easily isolated and recognized. A portion of the distillate mentioned was added to an ethereal solution of urethane. No reaction took place until after the ether had been distilled off and the heating on the water-bath continued for ten minutes. After the evolution of hydrochloric acid, which further heating produced, had ceased, the mixture solidified on cooling. This solid, washed and dried, melted at 190°. After recrystallization it was analyzed and found to be ethyl allophanate.

0.2420 gram substance gave 47 cc. moist nitrogen at 742 mm. and 24.5°

	Calculated for $C_4H_8N_2O_3$.	Found.
N	21.21	21.30

[1] Ann. Chem. (Liebig), **244**, 29. [2] Gattermann: *Ibid.*
[3] Gattermann: *Ibid.*

As Schroeter and Livinsk[1] had attempted to prepare allophanic ether by the action of phosphorus oxychloride on urethane, and had found that none was formed, it seemed here that the formation of allophanic ether must have been due to the presence of chlorformamide in the above distillate. It was thought best, however, to repeat the work of Schroeter and Livinsk and, on heating molecular quantities of urethane and phosphorus oxychloride on the water-bath, I obtained quite different results from those published by these chemists. Hydrochloric acid soon began to come off, and, on removing the unchanged urethane and phosphorus oxychloride with water, a residue remained from which allophanic ether was obtained and identified as usual.

The formation of allophanic ether in the action of urethane on the unknown chloride obtained by distilling a mixture of urethane and phosphorus pentachloride does, therefore, not prove the presence of chlorformamide in the distillate, while the other experiments described leave little doubt that no chlorformamide is formed in the reaction. From the results of a study of the action of phosgene on urethane, which will presently be described, and which showed the amide group in urethane to be most sensitive to reaction, it seems probable that when phosphorus pentachloride acts on urethane, besides forming as with other urethanes the chlorformamide complex, it introduces at the same time a phosphoric acid radical into the amide group, giving derivatives of the nature of, *e. g.*, $Cl_2P(NHCOCl)_3$ or $Cl_2PO(NHCOCl)$, etc. Such substances would give carbon dioxide with water, (40–70 per cent. as much as an equal weight of chlorformamide) and would give no phenylurea with aniline, nor urethane with alcohol.

III. ACTION OF PHOSGENE ON URETHANE.

One of the chief difficulties encountered in the study of the action of phosphorus pentachloride on urethane being the removal of phosphorus oxychloride from the reaction-product, phosgene, which has been used in similar cases[2] in place of phosphorus pentachloride because it gives only gaseous by-products, was brought into action with urethane. Its action

[1] Ber. d. chem. Ges., **26**, 2171. [2] Kempf: J. prakt. Chem. [2], **1**, 402.

on urethane might be analogous to the action of phosphorus pentachloride on phenylurethane, and thus give chlorformamide:

$$NH_2COOC_2H_5 + COCl_2 = NH_2COCl + CO_2 + C_2H_5Cl.$$

The only previous work[1] done on the action of phosgene on urethane rather indicated that such is the primary reaction. Loeb obtained from phosgene in benzene solution and a large excess of urethane, allophanic ether, as sole product, the very substance which chlorformamide forms in presence of an excess of urethane.[2]

Loeb, in the brief notice he published on the reaction, suggested that the allophanic ether could be formed by abstracting one molecule of alcohol from two molecules of urethane without indicating in what way such a reaction might take place. He also suggested another explanation for the formation of allophanic ether; *viz.*, that it might be a decomposition-product of a hypothetical intermediate substance, carbonyl diurethane, $CO(NHCOOC_2H_5)_2$, which was not obtained, but which he supposed might have been formed and then been decomposed by recrystallization from alcohol or chloroform, losing alcohol and carbon dioxide, and giving allophanic ether.

I varied the conditions of Loeb's reaction somewhat, using undiluted phosgene, and, in order to fulfil the above equation, equal molecules of phosgene and urethane were brought into action. 5 grams phosgene and 4 grams urethane were heated in a sealed tube to 75° for half an hour. When the tube was opened the escaping gas was collected in a nitrometer over sodic hydrate solution. The gas burned with the greenish flame of ethyl chloride. The contents of the tube were then rinsed into a flask with a small amount of benzene and cold, dry ligroïn added. A small amount of a colorless oil (A) was precipitated. Its color resembled that of the other urea chlorides. A part of this oil was added to aniline. The reaction with aniline was very violent and a white solid was obtained. The substance was washed with dilute hydrochloric acid and, recrystallized from hot water and from dilute alcohol, it melted sharply at 106°. Analysis showed it to have the composition $C_{10}H_{12}N_2O_3$.

[1] Loeb: Ber. d. chem. Ges., 19, 2344. [2] Gattermann: *loc. cit.*

I. 0.2563 gram substance gave 31.3 cc. moist nitrogen at 741.7 mm. and 21°.

II. 0.2159 gram substance gave 0.454 gram CO_2 and 0.1162 gram H_2O.

	Calculated for $C_{10}H_{12}N_2O_3$.	Found.
N	13.46	13.62
C	57.69	57.35
H	5.77	5.98

The formula $C_{10}H_{12}N_2O_3$ corresponds to that of phenylallophanic ether, which could have been formed as follows:

$$NH_2COOC_2H_5 + COCl_2 = ClOCNHCOOC_2H_5 + HCl.$$

$$C_2H_5O_2CNHCOCl + NH_2C_6H_5 = C_6H_5NHCONHCOOC_2H_5 + HCl.$$

Stojenten,[1] however, who prepared phenylallophanic ether, by the action of ethoxal chloride on monophenyl urea, gives its melting-point as 120°. Another quantity of the above compound was, therefore, prepared and purified by dissolving in sodic hydrate and precipitating it in the filtrate with hydrochloric acid and then recrystallizing the dry substance from ether and ligroïn. It still melted sharply at 106° and the analyses confirmed the composition $C_{10}H_{12}N_2O_3$.

I. 0.1653 gram substance gave 0.3492 gram CO_2 and 0.0868 gram H_2O.

II. 0.1605 gram substance gave 0.3388 gram CO_2 and 0.0849 gram H_2O.

	Calculated for $C_{10}H_{12}N_2O_3$.	Found. I.	Found. II.
C	57.69	57.61	57.57
H	5.77	5.83	5.87

In view of the discrepancy between the melting-point found by Stojenten and by myself it was decided to prepare phenylallophanic ether synthetically.

Synthesis of Phenylallophanic Ether, $C_6H_5NHCONHCOOC_2H_5$. —It was expected that phenyl isocyanate would readily take up urethane and give phenylallophanic ether,

$$C_6H_5NCO + H_2NCOOC_2H_5 = C_6H_5NHCONHCOOC_2H_5.$$

It was found, however, that phenylisocyanate and urethane

[1] J. prakt. Chem. [2], **32**, 18.

react only with great difficulty and in a different manner. Molecular quantities were heated to 55° for one hour, and to 160° for one hour; but in no case could allophanic ether be obtained. A mixture of two substances, one melting at about 173° and the other at about 195°, was formed; but these were not further examined; they are probably cyanuric acid derivatives.

A much smoother reaction results if chlorformanilide, $C_6H_5NHCOCl$, the hydrochloric acid addition-product of phenyl isocyanate, is substituted for the latter. 1.5 grams chlorformanilide (1 mol.) and 0.86 gram urethane (1 mol.) were heated to 100° for half an hour. The contents had still a strong odor of isocyanate, but solidified on cooling. The substance was purified by precipitation from alkaline solution and recrystallized from alcohol. The phenylallophanic ether obtained according to the equation,

$$C_6H_5NHCOCl + H_2NCO_2C_2H_5 = C_6H_5NHCONHCO_2C_2H_5 + HCl,$$

melted sharply at 106°, and when this synthetic product was mixed with the compound $C_{10}H_{12}N_2O_3$ above referred to its melting-point was not changed. This compound is, therefore, phenylallophanic ether, and the low melting-point is undoubtedly the correct one.[1] Stojenten's phenylallophanic ether was separated from phenylparabanic acid (melting-point 208°) by fractional precipitation, and it is possible that he mistook a mixture for pure phenylallophanic ether.

In order to show that the oil (*A*) from which phenylallophanic ether was obtained by means of aniline was not a mixture simply of unchanged urethane and phosgene, which could give phenylallophanic ether according to the equation,

$$C_6H_5NH_2 + COCl_2 + H_2NCOOC_2H_5 = 2HCl + C_6H_5NHCONHCO_2C_2H_5,$$

but contained chlorformylurethane, I dissolved a mixture of aniline and urethane in benzene, and added phosgene. The mixture reacted very violently, and carbanilide (melting-point 235°) was obtained, but not a trace of phenylallophanic ether. This proves that the formation of phenylallophanic ether in

[1] *Vide* analyses.

the above reaction with aniline is due to the presence of a chloride, $C_3H_4O_2CNHCOCl$, *chlorformylurethane*, which is formed from phosgene and urethane, as follows:

$$NH_2COOC_2H_5 + COCl_2 = C_3H_5O_2CNHCOCl + HCl.$$

The presence of chlorformylurethane in the oil *A* was confirmed by converting it by means of ammonia into allophanic ether. The oil *A*, as shown below, contains a very small quantity of allophanic ether, from 10 grams phosgene and 8 grams urethane, half a gram of allophanic ether being obtained. If the oil *A* be divided into two equal portions and dry ammonia be passed into one portion dissolved in benzene, this will give about 6 grams allophanic ether (melting-point 192°), while the other portion, treated in exactly the same way, but without passing ammonia into it, gives only about half a gram of allophanic ether. The allophanic ether is formed as follows:

$$C_3H_4O_2CNHCOCl + NH_3 = C_3H_5O_2CNHCONH_2 + HCl,$$

confirming the presence of chlorformylurethane in the oil *A*.

Besides this substance, the oil *A* contains at least two others. A part of this oil obtained from the first action of phosgene on urethane was left in a desiccator. On standing, this soon became somewhat turbid, and a white solid gradually formed until it consisted of a semi-solid mixture. Water was carefully added, and the mixture extracted with cold ether. From this ether-extract was obtained a small amount of a white crystalline compound which was recrystallized from ether and ligroïn and melted at 107°.

I. 0.1582 gram substance gave 18.8 cc. moist nitrogen at 755.2 mm. and 16.5°.

II. 0.1900 gram gave 0.2902 gram CO_2 and 0.1046 gram H_2O.

	Calculated for $C_7H_{12}N_2O_5$.	Found. I.	Found. II.
N	13.73	13.78	....
C	41.18	....	41.66
H	5.88	....	6.10

The analysis show this substance to have the composition $C_7H_{12}N_2O_5$, corresponding to carbonyldiurethane,

$$CO\begin{matrix}/NHCOOC_2H_5\\ \backslash NHCOOC_2H_5\end{matrix}.$$

It is formed by the action of the chloride $C_2H_5O_2CNHCOCl$, on a second molecule of urethane,

$$C_2H_5O_2CNHCOCl + H_2NCO_2C_2H_5 = CO\begin{matrix}/NHCOOC_2H_5\\ \backslash NHCOOC_2H_5\end{matrix} + HCl,$$

and is the carbonyldiurethane, which Loeb thought might be formed in his reaction, as an unstable intermediate product, and, on being recrystallized, give allophanic ether with loss of carbon dioxide and alcohol, but which had never been obtained before this.

Carbonyldiurethane is, as a matter of fact, a very stable substance. It suffers no decomposition on being recrystallized from any organic solvent or from water. It was heated in a sealed tube with a benzene solution of hydrochloric acid to 75°–80° for half an hour without change. Carbonyldiurethane cannot, therefore, be considered as an intermediate product in the formation of allophanic ether, as supposed by Loeb, but is one of the final products of the action of undiluted phosgene on urethane.

In the oil *A* there is a small quantity of a third substance, as already mentioned, *viz.*, allophanic ether. It remained after the carbonyldiurethane had been extracted with ether, and was recrystallized from alcohol, and identified by its melting-point (192°) which remained unchanged, when the substance was mixed with synthetic allophanic ether. Since carbonyldiurethane is perfectly stable and is not converted into allophanic ether under the conditions described, the formation of allophanic ether is best explained as follows: Besides acting on the amide group of urethane, phosgene, in a secondary reaction, splits off alcohol from urethane, the cyanic acid formed uniting at once with the liberated hydrogen chloride, giving chlorformamide. This in turn yields with a second molecule of urethane allophanic ether,[1]

[1] Gattermann: *Loc. cit.*

$NH_2COOC_2H_5 + COCl_2 = NH=CO + CO_2 + HCl + ClC_2H_5$,

$NH_2COCl + H_2NCOOC_2H_5 = NH_2CONHCO_2C_2H_5 + HCl$.

This view is strongly supported by the fact that allophanic ether is obtained from urethane, indifferently by using a number of similar chlorides as thionyl chloride,[1] phosphorus oxychloride,[2] and, as a by-product, even in the action of benzoyl chloride on urethane,[3] where the main product is also benzoylurethane, $C_6H_5CONHCO_2C_2H_5$, as with phosgene. The above explanation satisfies all of these cases.

The action of phosgene on urethane is, therefore, threefold, as may be briefly summarized by the following equations:

To a limited extent we have

(1) $NH_2COOC_2H_5 + COCl_2 = NH_2COCl + ClC_2H_5 + CO_2$,

$NH_2COCl + NH_2COOC_2H_5 = NH_2CONHCOOC_2H_5 + HCl$.

To a far greater extent we have

(2) $COCl_2 + NH_2COOC_2H_5 = ClCONHCOOC_2H_5 + HCl$.

This chloride, being also quite reactive, acts on a second molecule of urethane, so that we have also

(3) $C_2H_5OOCNHCOCl + NH_2COOC_2H_4 = CO(NHCO_2H_5)_2 + HCl$.

Carbonyldiurethane, $CO(NHCOOC_2H_5)_2$.—If in accordance with the last two equations two molecules of urethane be taken to one of phosgene, and the mixture heated to 85° for half an hour, the yield of diurethane is very largely increased. The best yield was obtained as follows: To two molecules of urethane and from one to two molecules of pyridine[4] was added one molecule of phosgene, contained in a loosely-stoppered tube so as to prevent any action taking place, before sealing the larger tube. The mixture was heated to 85° for thirty minutes, and the contents washed out with a small quantity of water. The water dissolved the pyridine and the pyridine hydrochloride, precipitating nearly all the carbonyldiurethane in a very pure condition. About eight grams diurethane was obtained from ten grams phosgene by

[1] Schroeter and Levinsk: Ber. d. chem. Ges., **26**, 2171. [2] *Vide* p. 343, (this paper).
[3] Pechmann and Vanino: Ber. d. chem. Ges., **28**, 2383.
[4] *Vide* Pechmann and Vanino: *loc. cit.*

this method. Carbonyldiurethane consists of white plates, and is very soluble in all the organic solvents except ligroïn. It is also readily soluble in hot water and in alkalies.

Silver Carbonyldiurethane, $AgOC\begin{matrix}/NCOOC_2H_5\\\backslash NHCOOC_2H_5\end{matrix}$. —From the solution of carbonyldiurethane in alkalies a silver salt can be prepared by precipitating with silver nitrate. The silver salt contains only one atom of silver to each molecule of carbonyldiurethane; my attempts to make it take up two atoms of silver were all unsuccessful. If the compound be dissolved in dilute caustic potash solution containing two molecules potassic hydrate, or a little more than one molecule, the white precipitate which is produced by each drop of silver nitrate solution is at once mixed with the brown oxide of silver. With the ammonia solution of carbonyldiurethane silver nitrate gives no precipitate.

The best method for preparing the pure silver salt I found to be the following: Diurethane was dissolving in dilute caustic potash solution containing a trifle less than one molecule potassic hydrate. Silver nitrate solution in excess was then added with constant stirring. A bulky, gelatinous precipitate, which is very difficult to wash, is thus formed. The mixture was, therefore, left standing in a dark place for twelve hours; the precipitate remained perfectly white. It was then filtered, and washed with cold water and dried in a desiccator. The dry salt was powdered and again washed very thoroughly with cold water, being kept in the dark as much as possible. By this method I obtained the salt pure, and very little colored. A small amount of alkali is liable to cling to it with the greatest tenacity, and cannot be removed from the freshly prepared, gelatinous salt, either by cold or by hot water. The salt is, besides, somewhat soluble in hot water, and to some extent decomposed by it. 4.9 grams of this pure salt was obtained from 4 grams carbonyldiurethane.

I. 0.2488 gram substance gave 0.2441 gram CO_2 and 0.0858 gram H_2O.

II. 0.3191 gram substance gave 26.4 cc. moist nitrogen at 740.2 mm. and 27.5°.

III. 0.3918 gram substance gave 0.13673 gram Ag.

	Calculated[1] for $C_7H_{11}N_2O_2Ag$.	Found.
C	27.04	26.76
H	3.54	3.83
N	9.01	8.92
Ag	34.66	34.90

The results obtained in the experiments described in this paper may be summarized as follows:

(1) The reaction

$$RCONHBr + NaOCH_3 = RNHCOOCH_3 + NaBr,$$

is quite as general as the analogous reaction of alkalies on acid bromamides, and should be quite as useful in the preparation of urethanes as is the reaction of Hofmann in the preparation of amines. The introduction of negative groups into the radical R does not prevent the "Beckmann rearrangement" of the acid bromamides by sodium methylate with the formation of urethanes, and in no case was direct substitution of the bromine atom effected even to a slight extent. This result is in entire accord with the results of Hoogewerff and Van Dorp with aqueous alkalies. The introduction of positive groups, as far as determined by the single case where such a bromamide was examined, has no more influence than that of negative groups.[2]

(2) The reaction of phosphorus pentachloride on urethanes according to the equation

$$RNHCOOCH_3 + PCl_5 = RNHCOCl + CH_3Cl + POCl_3$$

is also general in the urethanes of the aromatic amines.

The above two reactions together give easy methods for preparing chlorformanilides and isocyanates. The chlorformanilides thus prepared are often much more reactive than the corresponding isocyanates, as shown in the synthesis of phenylallophanic ether, and can be used with advantage in their place.

(3) With free urethane, $NH_2COOC_2H_5$, phosphorus pentachloride splits off ethyl chloride and a carbamide chloride is

[1] NOTE.—Mr. F. B. Dains, working under the direction of Dr. Stieglitz, is studying the constitution of this silver salt, and has already obtained an alkyl derivative corresponding to the constitution indicated.

[2] The investigation on the effect of positive groups is being continued in this laboratory.

formed; but the reaction is not so simple as with the aromatic urethanes; the phosphoric chloride most likely enters the amide group, giving phosphoric acid derivatives of chlorformamide.

(4) Phosgene and urethane when brought together in molecular proportions react simultaneously in three different ways:

1. $NH_2COOC_2H_5 + COCl_2 = ClCONHCOOC_2H_5 + HCl$.
2. $ClCONHCOOC_2H_5 + H_2NCOOC_2H_5 = CO(NHCOOC_2H_5)_2 + HCl$.
3. $2NH_2COOC_2H_5 + COCl_2 = NH_2CONHCOOC_2H_5 + ClC_2H_5 + CO_2 + HCl$.

The first two reactions can be regulated to a large extent by adding an excess of one or the other of the reacting substances. The third reaction, on the other hand, occurred to a small extent in all the reactions of phosgene on urethane as it apparently does in the action of any acid chloride on urethane.

The above investigations were pursued under the direction of Dr. Stieglitz, and I wish here to express my sincere appreciation of the thoughtfulness with which he guided and assisted me in the work.

ACTION OF PHOSPHORUS PENTACHLORIDE ON ANILINE AND ITS SALTS.

By J. Elliott Gilpin.

The constant occurrence of chlorphosphuret of nitrogen ($PNCl_2$)$_x$ as a by-product in the formation of orthosulphobenzoic acid from commercial saccharine directed attention in this laboratory to this very interesting substance. Discovered by Liebig, it was studied by Liebig and Wöhler,[1] Gladstone and Holmes,[2] Laurent,[3] Wichelhaus,[4] Hofmann,[5] and Stokes.[6] Hofmann studied its action with aniline and paratoluidine, and obtained derivatives in which the chlorine had been replaced by residues of aniline and paratoluidine, the product

[1] Ann. Chem. (Liebig), **11**, 139.
[2] Ann. Chem. (Liebig), **76**, 74.
[3] Compt. Rend., 1850, Sep. (9).
[4] Ber. d. chem. Ges., **3**, 163.
[5] Ber. d. chem. Ges., **16**, 1910.
[6] This Journal, **17**, 275.

with the aniline having the composition $P_3N_3(NHC_6H_5)_4$. Besson[1] has repeated the work done on this substance and obtained the compound $PNCl_2$. He says the compound described by Gladstone as having the composition $(PNCl_2)_3$ and the melting-point 210° is probably a polymeric form of $PNCl_2$; but there is evidently some mistake here, as Gladstone found the melting-point to be 110° and not 210°, while according to Besson it is 114°. As the formation of the chlorphosphuret of nitrogen is due to the action of phosphorus pentachloride on ammonium chloride, the possibility was suggested of obtaining a derivative of it by using instead of ammonium chloride a substitution-product, aniline hydrochloride. Although the substance obtained in this action is not a derivative of the chlorphosphuret of nitrogen, still a comparison of the two forms an interesting study. They show the tendency of phosphorus and nitrogen to combine sometimes in a very stable form as in the chlorphosphuret of nitrogen and a substance obtained in this investigation, which will be discussed later. The former can be heated with concentrated acids and alkalies without undergoing change; but the trichlorphosphanil, obtained in this work, is very unstable, decomposing with nearly all reagents, and even slowly when exposed to moisture.

Up to the time when this investigation was begun the study of the action of aniline on the chlorides of phosphorus had not led to satisfactory results, and the action with the trichloride only had been studied. By the action of aniline on phosphorus trichloride, Tait[2] obtained a compound to which he gave the formula $P(NH_2C_6H_4Cl)_3$. Jackson and Menke[3] repeated this work, but were unable to obtain the product described by Tait. They obtained a product which they thought had the composition $PCl(NHC_6H_5)_2$, but were unable to isolate it. By dissolving it in alcohol and precipitating with water they obtained the compound $P(OH)(NHC_6H_5)_2$, which they considered to be its hydroxyl derivative. Weyer[4] studied the action of aniline on trichloride of arsenic, and obtained two definite products by the successive substitution of

1 Compt. Rend., **114**, 1264.
2 Ztschr. Chem., 1865, 648.
3 This JOURNAL, **6**, 89.
4 Dissertation, Bonn, 1891.

aniline residues for the chlorine atoms. These were represented by the formulas $AsCl_3(NHC_6H_5)$ and $AsCl(NHC_6H_5)_2$. The third step he was unable to take. In the present investigation, in which the action of phosphorus pentachloride on aniline and its salts is under investigation, four definite substances have been isolated. They are formed by the substitution of residues of aniline for one or more chlorine atoms of the phosphorus pentachloride, one being obtained by the action of phosphorus pentachloride on aniline hydrochloride, and three by the action on aniline. The trichlorphosphanil, having the composition $PCl_3(NC_6H_5)$, which was obtained from the aniline hydrochloride, shows great similarity to the first derivative obtained by Weyer. They are both very sensitive to moisture, and decompose with water and alcohol in a similar manner. The other substances were more stable, and were obtained from their solutions in alcohol in the form of well-defined crystals.

During the progress of this investigation an article by Michaelis and Schroeter[1] has appeared, in which a substance, formed by the action of aniline on phosphorus trichloride, of the composition $C_6H_5N—PCl$, is described. This substance bears the same relation to phosphorus trichloride, as the trichlorphosphanil, described in this paper, does to phosphorus pentachloride.

Action of Phosphorus Pentachloride on Aniline Hydrochloride—Trichlorphosphanil $PCl_3(NC_6H_5)$.

After considerable experimenting, the following method was adopted as the best for the preparation of this substance: Phosphorus pentachloride and perfectly dry aniline hydrochloride are mixed in molecular quantities, not more than ten grams of the aniline hydrochloride being used at a time. The intimately mixed compounds are placed in a distilling-bulb, and connected with a condenser. A tube at the lower end of the condenser passes into a vessel of water, to absorb the hydrochloric acid formed, and show the rate of the action. The bulb is half immersed in a sulphuric-acid bath. Before the temperature at which the trichlorphosphanil is formed is

[1] Ber. d. chem. Ges., 27, 490.

reached, a small quantity of phosphorus pentachloride sublimes in the upper part of the neck. If the temperature is kept at 170° for six to eight hours, the trichlorphosphanil condenses on the cool part of the bulb, and sometimes in the condenser, as a white coating, covered on the inside with nodules. After the evolution of hydrochloric acid has ceased, the material can be obtained in a very pure condition, if the part in the neck of the bulb is discarded. After being powdered, it is placed in a desiccator over caustic potash to remove the hydrochloric acid. It must be kept perfectly dry, and cannot be purified by crystallization, as water, alcohol, ether, acetone, and other solvents decompose it. Even when resublimed some decomposition takes place. In every case there was a small quantity of a dark, green, sticky material left in the bulb after the action was over. This may have been due to impurities in the phosphorus pentachloride, as the ordinary commercial article was used. When heated with water this green material acts quite violently at first, in consequence no doubt of the presence of a small excess of phosphorus pentachloride, and a tar-like mass is formed, which is unacted on by water, alkali, and dilute acid, and solidifies on cooling. It is soluble in alcohol, with a green color; so some was dissolved in alcohol and precipitated by addition of water, filtered and washed. This was repeated several times, and the green powder obtained was analyzed; but different preparations varied in composition, and it was evidently not a single definite compound.

The formation of the trichlorphosphanil probably takes place as represented in the following equation:

$$PCl_5 + C_6H_5NH_2HCl = PCl_3(NC_6H_5) + 3HCl.$$

Concentrated sulphuric and nitric acids both decompose it, the former with the evolution of hydrochloric acid. Alcohol and ether act on it with the evolution of hydrochloric acid and the generation of considerable heat. Sodium hydroxide acts on it to a slight extent, and changes it to a hard, brittle mass. When boiled with water it is decomposed into aniline, hydrochloric and phosphoric acids, so that the chlorine and phosphorus can be determined in the same specimen, the

chlorine as silver chloride, and the phosphorus as magnesium pyrophosphate. To be sure that none of the hydrochloric acid was lost in boiling, several determinations were made by the Carius method, but they agreed with those made in the other way.

The following are the results of the analyses:

Preparation I.

0.3662 gram of the substance gave 0.6754 gram AgCl.

0.2848 gram of the substance gave 0.5226 gram AgCl.

0.2560 gram of the substance gave 0.4672 gram AgCl.

0.3662 gram of the substance gave 0.1788 gram $Mg_2P_2O_7$.

0.2848 gram of the substance gave 0.1367 gram $Mg_2P_2O_7$.

0.2560 gram of the substance gave 0.1242 gram $Mg_2P_2O_7$.

0.2755 gram of the substance gave 0.0609 gram H_2O and 0.3196 gram CO_2.

0.4078 gram of the substance gave 22 cc. N at 16° and 772.5 mm.

Preparation II.

0.2568 gram of the substance gave 0.4635 gram AgCl.

0.3535 gram of the substance gave 0.6354 gram AgCl.

0.3535 gram of the substance gave 0.1695 gram $Mg_2P_2O_7$.

0.4237 gram of the substance gave 23 cc. N at 11°.5 and 762 mm.

0.3698 gram of the substance gave 0.0765 gram H_2O and 0.4081 gram CO_2.

0.3646 gram of the substance gave 0.0748 gram H_2O and 0.4078 gram CO_2.

	Calculated for $PCl_2(NC_6H_5)$.	Found.					
		Preparation I.			Preparation II.		
C	31.55	....	31.63	....	30.09	....	30.50
H	2.19	....	2.45	....	2.29	....	2.27
Cl	46.53	45.59	45.36	45.11	44.43	....	44.61
P	13.58	13.64	13.41	13.56	....	13.40	....
N	6.17	....	6.38	....	....	6.47	....

While these results leave much to be desired, they point clearly to the formula given, and are fairly satisfactory, considering the instability of the substance.

The sulphate and nitrate of aniline were also treated with

phosphorus pentachloride, but they did not act like the hydrochloride. The action of the nitrate was very violent, taking place as soon as they were mixed, without the aid of heat. The whole mass was carbonized in a short time. Paratoluidine hydrochloride was also treated with phosphorus pentachloride, but no volatile product was formed.

Decomposition of Trichlorphosphanil with Water.

When trichlorphosphanil is heated with water it first melts and forms an oil which is decomposed by further boiling. The decomposition gives rise to the formation of aniline, and hydrochloric and phosphoric acids, and can be represented thus:

$$PCl_3(NC_6H_5) + 4H_2O = C_6H_5NH_2.HCl + 2HCl + H_3PO_4.$$

The crystals which separated out, after decomposing with water and evaporating, were recrystallized and analyzed. The results of the analyses showed it to be aniline hydrochloride. Another portion was decomposed with water, an excess of barium hydroxide added to liberate the aniline, and this then distilled off. After filtering off the excess of the hydroxide, the presence of barium chloride was proved, showing that free hydrochloric acid had been present. The barium was precipitated with sulphuric acid and the phosphoric acid obtained by evaporating the solution.

Decomposition of Trichlorphosphanil with Sulphuric Acid.

Trichlorphosphanil dissolves in warm concentrated sulphuric acid, with evolution of hydrochloric acid gas. An equal volume of water is added to this, and the liquid is allowed to stand, when a substance crystallized out which was found to be sulphanilic acid. Several of its salts were made and analyzed.

Action of Phosphorus Pentachloride on Aniline. Chlorphostetranilide, $PCl(NHC_6H_5)_4$.

When phosphorus pentachloride is slowly added to aniline and the mass constantly stirred, there is immediate action and hydrochloric acid is evolved. The whole mass becomes hot, and after all the aniline has been used up, and further

addition of phosphorus pentachloride causes no action, it solidifies. This mass, when cool, is broken up and heated with water to extract any aniline hydrochloride and phosphorus pentachloride present, then filtered, washed, and dried. This product, which is a light-yellow powder, is insoluble in water, but slightly soluble in alcohol. It consists largely of one substance, but several others are present in small quantities.

If the dried mass is shaken with two separate quantities of cold alcohol, and the liquid, after being filtered, is allowed to evaporate slowly, besides some needle-shaped crystals there will be found some well defined monoclinic crystals, which grow to a considerable size. These have to be separated from the other product mechanically. If the solution from which these have been obtained is filtered and allowed to evaporate still further, in some cases, tufts of fine, radiating, silky needles separate out. Both these and the large crystals will be discussed later. After treating several times with cold alcohol, the original material is treated repeatedly with small quantities of hot alcohol, until on evaporation only one substance separates out from the solution. By this process a definite substance is obtained in pure condition. This is slightly soluble in alcohol and insoluble in water. When crystallized from alcohol it usually consists of long, irregular-shaped crystals; but, when the evaporation is very slow, and absolute alcohol is used, monoclinic crystals with well defined basal planes and fundamental prisms, are formed. The composition of this substance is represented by the formula $PCl(NHC_6H_5)_4$, and its mode of formation is expressed as follows:

$$PCl_5 + 4C_6H_5NH_2 = PCl(NHC_6H_5)_4 + 4HCl.$$

It is not decomposed when boiled with water, concentrated alkali, or hydrochloric acid; but when heated with water in a sealed tube to 180° for several hours, aniline, aniline hydrochloride, and phosphoric acid are formed. This substance is characterized by its great insolubility. It is practically insoluble in ethyl ether, acetone, benzene, ligroïn, and amyl alcohol; but slightly soluble in ethyl alcohol. When heated, a

volatile product, which proved to be a mixture of aniline, aniline hydrochloride, and some diphenylamine hydrochloride, formed by the action of aniline on aniline hydrochloride, was formed, and an amorphous black substance remained. The great stability of this substance is shown by the fact that *only a small amount was decomposed when it was heated in a porcelain tube, in a current of oxygen, over the blast-lamp for several hours.*

A qualitative analysis of this substance showed that it contains phosphorus, nitrogen, and carbon. The black stable residue is very similar to a product described by Rose.[1] By the action of phosphorus trichloride on ammonia he obtained a product to which he gave the formula $PCl_3 + 5NH_3$. When this was heated, ammonium phosphate and ammonium chloride were formed, and a white substance, phospham, PN_2H, was left behind. A comparison of this and the black residue is worthy of notice. Neither is soluble in water or dilute acids. They are only partly decomposed by boiling with fuming nitric acid for some time. Concentrated sulphuric acid attacks the phospham; but acid potassium sulphate is necessary to decompose the black residue. Neither is acted on when heated in a stream of chlorine. They are decomposed by fused alkali, and also with generation of phosphorus or a compound of phosphorus and hydrogen, when heated to redness in a current of hydrogen. The black residue may also contain a small amount of hydrogen; but this cannot be considered as certain, for the decomposition of the substance is accomplished with so great difficulty that the sources of error introduced may account for the presence of the hydrogen.

The formation of this compound prevented the determination of the carbon and hydrogen by the usual method in the case of all the compounds studied, except that of the trichlorphosphanil, which is volatile. In some cases, when the substances were heated in platinum boats, a transparent film was formed about the small particles of carbon, preventing their complete combustion. The method finally adopted for the determination of carbon, and the only one by which satis-

[1] Ann. der. phys. Pogg., **28**, 529; Ann. Chem. (Liebig), **11**, 130.

factory results could be obtained, was that described by Fritsch,[1] in which the substance was oxidized by potassium chromate and sulphuric acid.

The nitrogen was determined both by the absolute and by the Kjeldahl methods. The chlorine and phosphorus were determined as silver chloride and magnesium pyrophosphate respectively, the substance being decomposed by heating it with fuming nitric acid in a sealed tube to 180° for several hours.

Analysis of the Dry Powder.

Preparation I.

The specimen of aniline used for this was not purified and was very dark, and the products retained some of the impurities.

0.2332 gram of the substance gave 0.0746 gram AgCl.
0.19765 gram of the substance gave 0.0631 gram AgCl.
0.2102 gram of the substance gave 0.0553 gram $Mg_2P_2O_7$.
0.154 gram of the substance gave 0.3724 gram CO_2.
0.1974 gram of the substance gave 0.4784 gram CO_2.

Preparation II.

0.2366 gram of the substance gave 0.0784 gram AgCl.
0.2366 gram of the substance gave 0.0595 gram $Mg_2P_2O_7$.
0.2096 gram of the substance gave 0.0691 gram AgCl.
0.2096 gram of the substance gave 0.0552 gram $Mg_2P_2O_7$.
0.488 gram of the substance 0.0633144 gram N (Kjeldahl).
0.189 gram of the substance gave 22.23 cc. N. at 25.8° and 758.8 mm.
0.1584 gram of the substance gave 0.3863 gram CO_2.

Preparation III.

0.1966 gram of the substance gave 0.0655 gram AgCl.
0.2025 gram of the substance gave 0.494 gram CO_2.

Analyses of the Crystals.

0.2258 gram of the substance gave 0.057 gram $Mg_2P_2O_7$.
0.2309 gram of the substance gave 0.0792 gram AgCl.
0.2309 gram of the substance gave 0.0612 gram $Mg_2P_2O_7$.

[1] Ann. Chem. (Liebig), **294**, 79.

0.2324 gram of the substance gave 0.0792 gram AgCl.
0.1613 gram of the substance gave 0.0553 gram AgCl.
0.1613 gram of the substance gave 0.0435 gram $Mg_2P_2O_7$.
0.1483 gram of the substance gave 0.0503 gram AgCl.

	Calculated for $PCl(NHC_6H_5)_4$.	Found (powder). Preparation I.			II.		III.
Cl	8.14	7.90	7.89	...	8.19	8.14	8.24
P	7.13	...	...	7.44	7.02	7.36	...
N	12.89	...	...	...	12.97	13.04	...
		Found (crystals).					
Cl	8.14	....	8.47		8.42	8.47	8.38
P	7.13	7.05	7.40		...	7.53	...
N	12.89	....	...		...	...	...
C	66.29	65.94	66.09		...	66.50	66.52

Attempts made to substitute a residue of aniline for the chlorine atom in the compound, $PCl(NHC_6H_5)_4$, have up to the present been unsuccessful. Some of the powder was added to boiling aniline, in which it readily dissolved; but the product which separated out when it cooled had the same composition as the original material.

Action of Sulphuric Acid on Chlorphostetranilide, $PCl(NHC_6H_5)_4$.

When chlorphostetranilide is treated with concentrated sulphuric acid, hydrochloric acid is given off, and the substance goes into solution. If the acid is warmed and saturated with the tetranilide it becomes solid, with crystals, on cooling. The following method was used for the preparation of the compound formed in the action:

The tetranilide was treated with as small a quantity of sulphuric acid as possible, and the solution warmed to complete the decomposition and expel the hydrochloric acid. After cooling, water was added, in volume about twice that of the acid, and the solution heated to dissolve the substance precipitated by the water. This solution, on standing, deposits clear, octahedral crystals, which can be filtered off, and recrystallized from water. These crystals are extremely efflorescent, and begin to lose their water of crystallization before the water which they hold mechanically can be removed.

It has acid properties and is very soluble in water and alco-

hol, as are also the barium and lead salts, which are formed by neutralizing a solution of the acid with barium and lead carbonates, and filtering and evaporating the solutions.

On account of the ease with which these salts dissolve in water, they could not be obtained in a crystallized condition suitable for analysis, but in each case were evaporated to dryness over the water-bath. The action of the sulphuric acid on the tetranilide is as follows:

$$PCl(NHC_6H_5)_4 + 4H_2SO_4 = P(OH)(NHC_6H_4SO_3H)_4 + 3H_2O + HCl.$$

The sulphur and phosphorus were determined as barium sulphate and magnesium pyrophosphate, respectively. The substance was decomposed according to the Pierson method with nitric acid and potassium chlorate.

0.1518 gram of the substance gave 0.1927 gram $BaSO_4$.
0.2086 gram of the substance gave 0.0313 gram $Mg_2P_2O_7$.

	Calculated for $P(OH)(NHC_6H_4SO_3H)_4$.	Found.
S	17.39	17.44
P	4.21	4.19

The determinations of the barium and lead in the salts gave the following results:

0.4358 gram of the substance gave 0.1614 gram $BaSO_4$.
0.4499 gram of the substance gave 0.1694 gram $BaSO_4$.
0.6464 gram of the substance gave 0.2741 gram $PbSO_4$.
0.6333 gram of the substance gave 0.2676 gram $PbSO_4$.

These results cannot be explained on the assumption of the formation of a simple compound; but they agree with a salt of the following composition, in which part of the hydrogen of two molecules of the sulphonic acid is replaced by the metals:

$$P(OH)\begin{cases} NHC_6H_4SO_3H \\ NHC_6H_4SO_3 \\ NHC_6H_4SO_3 \\ NHC_6H_4SO_3 \end{cases} > x \quad \text{where } x = \text{barium or lead.}$$

$$P(OH)\begin{cases} NHC_6H_4SO_3 \\ NHC_6H_4SO_3 \\ NHC_6H_4SO_3 \\ NHC_6H_4SO_3H \end{cases} > x$$

	Calculated for these salts.	Found. 1.	2.
Ba	21.89	21.78	22.14
Pb	29.69	28.95	28.88

Action of Phosphorus Pentachloride on the Toluidines.

When the three toluidines are treated under the same conditions as the aniline, with phosphorus pentachloride, they give compounds analogous to chlorphostetranilide. The method of purification was the same as that used with the aniline compound. The results of the analyses were as follows:

Orthotoluidine.

0.2011 gram of the substance gave 0.0599 gram AgCl.

0.2888 gram of the substance gave 0.0692 gram $Mg_2P_2O_7$.

Metatoluidine.

0.213 gram of the substance gave 0.066 gram AgCl.

Paratoluidine.

0.2918 gram of the substance gave 0.0814 gram AgCl.

	Calculated.	Found. Ortho.	Meta.	Para.
Cl	7.21	7.36	7.65	6.89
P	6.32	6.69	...	...

Besides the compounds already mentioned, two other substances have been obtained by treating aniline with phosphorus pentachloride, under different conditions. The results of the investigation carried out on these substances, will be published shortly.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY,
March, 1897.

Contribution from the Sheffield Laboratory of Yale University.

L.—ON THE PREPARATION OF METABROMBENZOIC ACID AND OF METABROMNITROBENZENE.

BY H. L. WHEELER AND B. W. MCFARLAND.

It is now over thirty years since Reinecke[1] showed that benzoic acid could be directly brominated. His method was to heat the acid with bromine and water, in a closed tube, to

[1] Ztschr. Chem., 1865, 116; 1869, 109.

100° for several days. Reinecke's method, with the modifications of Hübner, Ohly, Philipp[1], Petermann,[2] and Angerstein[3] for its purification, is given in the last edition of Beilstein's *Handbuch* as the method of preparation ("Darstellung").

Again, according to the above authority, metabromnitrobenzene is best prepared as follows: (*i. e.*, "Darstellung"): "Man erhitzt in Röhren von 150 cc. Inhalt je 25 g. Nitrobenzol mit 32.5 g. (über H_2SO_4 entwässertem) Brom und 1 g. pulverisirten Eisenchlorid zwölf Stunden lang auf 60°–70°." This is Scheufelen's[4] method and it gives a yield of over 80 per cent. of the calculated quantity of pure metabromnitrobenzene.

Scheufelen also showed that ferrous bromide would readily effect the bromination in closed tubes. An experiment of his in an open vessel was not a success, however, since only 25 per cent. of the theoretical yield of metabromnitrobenzene was obtained.

The above methods can be greatly simplified, inasmuch as the operations can be performed in a short time and without the use of closed tubes if iron be used as a bromine carrier. Moreover, contrary to the result of Scheufelen, a yield of metabromnitrobenzene almost equal to that obtained in closed tubes with ferrous bromide, can be obtained in open vessels by the use of iron.

Iron, as a bromine-carrier, is now frequently used in other cases, since it often effects bromination with surprising readiness. This property of iron is well illustrated with paradichlorbenzene. (See below.) From the experiments with iron and ferrous bromide, in the case of nitrobenzene, it appears that iron is a better carrier of bromine than separately prepared ferrous bromide and naturally more convenient.

Metabrombenzoic Acid.—After a number of experiments we have come to the conclusion that the following is the best method for the preparation of this acid: 20 grams of benzoic acid and 6 grams of iron wire or gauze are placed together in a flask connected with a condenser and heated on a metal

[1] Ann. Chem. (Liebig), **143**, 233.
[2] *Ibid.*, **149**, 131.
[3] *Ibid.*, **158**, 5.
[4] *Ibid.*, **231**, 165.

bath. When the temperature of the bath reaches about 170° 48 grams of bromine are added, drop by drop, while the temperature of the bath is allowed to rise until at the end of the operation it reaches 260°. The addition of the bromine requires about one hour and a half, with the above quantities, when the bromination is finished. The quantity of bromine given is sufficient to convert all the iron into ferrous bromide, the benzoic acid into monobrombenzoic acid, and then allow 4.7 grams for loss. Generally, however, not all the iron is attacked and some dibrombenzoic acid results.

After the bromine has been added the mass is dissolved in sodium hydroxide, filtered from the iron and ferric hydroxide, and after precipitating the metabrombenzoic acid with hydrochloric acid it can then be purified in the usual way. We proceeded as follows in the purification: After precipitating the acid with hydrochloric acid it was shaken out with ether. This gave a crude product weighing 32 grams; calculated weight for monobrombenzoic acid, 32.9 grams. This was distilled and the portion boiling below 300° (none came over below 280°), and weighing 20 grams, was crystallized once from 50-per cent. alcohol. It melted from 145°–148° and was therefore practically pure metabrombenzoic acid. From this it will be seen that the yield of the acid does not lie far short of being equal to the weight of benzoic acid employed. The same material crystallized three times from benzene melted at 152°–153°, which is the melting-point usually assigned to the pure acid.[1]

Perbrombenzene, C_6Br_6.—An experiment in a closed tube gave perbrombenzene as the sole product. The carboxyl group of the acid being displaced, 5 grams of benzoic acid, 2 grams of iron, and 37.4 grams of bromine were heated in a tube to 225° for five hours. On opening the tube great pressure was observed and the bromine had entirely disappeared.

[1] Metabrombenzoic acid resembles benzoic acid in the manner in which its melting-point is lowered by a slight amount of impurity or admixture. Friedburg (Ann. Chem. (Liebig), **188**, 23) states that the pure acid melts at 155°, and that benzoic acid melts at 121°, while a mixture of these acids containing 20 per cent. of benzoic acid melts as low as 115°, and therefore 6° lower than benzoic acid. With larger amounts of impurities the melting-point of the mixture was observed as low as 96°, and, as Friedburg states: "Man sieht also, das man sich nicht wundern darf, bei der Bereitung der Brombenzoesäure niedrig schmelzende Gemische zu erhalten."

The crystalline product obtained was difficultly soluble in the ordinary solvents; from benzene it separated in the form of needles and did not melt below the boiling-point of sulphuric acid.

Metabromnitrobenzene.—30 grams of nitrobenzene and 3 grams of iron wire are placed in a flask with reversed condenser and heated up to 120° in an oil-bath. 60 grams of bromine are then gradually added, the operation taking about three-quarters of an hour. The flask is left in the bath for three-quarters of an hour more, and then the contents distilled in steam. The crude, almost pure, product thus obtained after pressing on paper and drying amounts generally to about 75 per cent. of the calculated. We have obtained a yield, however, as high as 85 per cent. by the above method. In one experiment using three times the above quantities a yield of 64 per cent. of the calculated was obtained. These results, although somewhat lower than the best obtained in closed tubes, are highly satisfactory when one considers the greater time required and the other disadvantage in the closed-tube method.

1,4-Dichor-2,5-dibrombenzene (?).—An experiment with paradichlorbenzene was interesting as a further illustration of the ease with which iron often effects bromination. Paradichlorbenzene, when pure, can be boiled with its own volume of bromine and the bromine all driven off without altering its melting-point or without its giving off hydrogen bromide. If, however, a piece of iron be added to the warmed mixture, a strong effervescence takes place, hydrogen bromide is given off, and the reaction proceeds of itself, the product soon solidifying. After pulverizing and washing out the iron bromide, the residue can be crystallized from hot absolute alcohol, in which it is difficultly soluble. It then gives beautiful colorless needles or prisms which melt at about 148°. A product thus obtained gave the following results on analysis:

	Found.	Calculated for $C_6H_2Cl_2Br_2$.
Cl	23.26	23.31
Br	52.33	52.46

This is presumably 1,4-dichlor-2,5-dibrombenzene, the

corresponding tetrabrombenzene which it resembles in regard to solubility, etc., being also formed by direct bromination. With the exception of the fact that it was found that this compound is very unreactive, it was not further investigated, test-tube experiments showing that it was not affected appreciably by boiling with nitric acid, and that it could be volatilized from fused sodium hydrate.

In conclusion, the authors desire to express their thanks to Messrs. W. M. Bradley, G. R. Tracy, and W. Valentine, who have assisted in the present work.

NEW HAVEN, FEBRUARY, 1897.

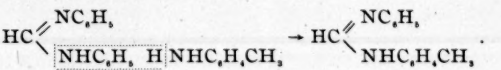
Contributions from the Sheffield Laboratory of Yale University.

LI.—ON THE NON-EXISTENCE OF FOUR METHENYLPHENYLPARATOLYLAMIDINES.

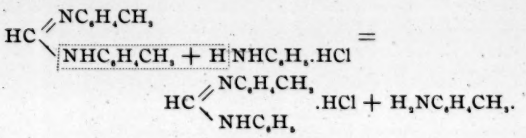
BY H. L. WHEELER.

In the first number of the Journal für praktische Chemie for this year, Walther[1] describes the preparation of methenylphenylparatolylamidine by four different methods. Each method, according to him, gave a new amidine, and these amidines were supposed to be isomers. The methods he used and the compounds he claims to have obtained are as follows:

I. By heating methenyldiphenylamidine with *p*-toluidine a product was obtained which melted at 120°. He explains the formation of this as follows:

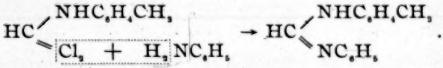


II. By boiling an alcoholic solution of methenyldiparatolylamidine with aniline hydrochloride a product melting at 132° was obtained:

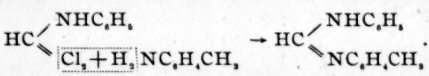


[1] Bd. **55**, 41.

III. By treating a mixture of *p*-formtoluide with aniline and phosphorus trichloride a product melting at 98° was obtained. He states that the following amidine is expected to result here :



IV. Finally he states that by reversing the above and treating a mixture of formanilide and *p*-toluidine with phosphorus trichloride a reaction as follows must take place, or, in other words, that an amidine with the following structure must result :



Walther concludes that two of these amidines are structural isomers while the others are perhaps physical modifications or stereochemical isomers.

The existence of four isomeric methenylphenylparatolylamidines is theoretically possible and would therefore not be remarkable, but that these four should be formed separately in the above reactions is not in harmony with the general behavior of amidines, imide chlorides,[1] or imidoesters, and that these substances should act by direct double decomposition, as indicated above, seems incredible. Moreover, these results are not in harmony with the careful work of Pechmann[2] on the amidines. Pechmann has shown in several cases that only one amidine results, when prepared from imide chlorides, where two might be expected.[3]

The re-examination of the above products was therefore

[1] Most probably imide chlorides are to be considered in reactions III and IV and not amide chlorides.

[2] Ber. d. chem. Ges., **28**, 869 and 2362.

[3] It may be stated here that seven years ago while the author was engaged in a research on the isoanilides with Mr. W. J. Comstock, it was observed that the same amidine resulted when prepared from phenylformimidomethyl ester and metanitraniline or from metanitrophenylformimidomethyl ester and aniline. The products obtained by these different methods were identical in regard to melting-point and general behavior. The preparation of this amidine by only one method was given at that time, the intention being to examine the subject more thoroughly and the work had just been resumed when Pechmann's article appeared.

undertaken with the result that all attempts to confirm the statements of Walther were unsuccessful. In no case, by the first and second method, were products obtained that melted constantly at 120° or 132°. Products were obtained that melted near these temperatures, and corresponded otherwise with Walther's descriptions, but, when crystallized, they proved to be nothing but impure methenyldiphenylamidine and methenyldiparatolylamidine, respectively.

According to the third and fourth method apparently one and the same methenylphenylparatolylamidine was obtained. This did not melt at 98° nor at 102° when purified by repeated crystallizations, but more nearly at 103°.5 to 104°, when prepared by the third method, and at 103°.5 to 104°.5, or practically at 104°, when prepared by the fourth method. The products could not be distinguished in appearance and properties except by this slight difference in melting-points. This difference in complete melting is to be explained by the fact that when this amidine is prepared by the third method, under certain conditions, an impurity accompanies the chief product, which it is difficult or impossible to separate by crystallizing from ligroïn. This impurity is probably methenyldiparatolylamidine.

The amidine melting at about 103°.5 is the true methenylphenylparatolylamidine, since the same compound results from paratolylformimidomethyl ester and aniline.

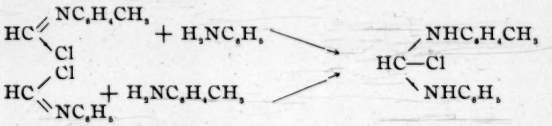
Walther comments on the products obtained by the third and fourth methods, as follows: "Allein an der Verschiedenheit beider Körper ist nicht zu zweifeln; beim Umkrystallisiren derselben aus warmem Petroläther ist der Unterschied in ihrem Verhalten schon deutlich ausgeprägt: der Körper vom Schmelzp. 98° löst sich leichter und fält beim Abkühlen der Lösung sofort in weissen Nadeln aus, der Körper von Schmelzp. 102° geht schwerer in Lösung und setzt sich langsam in harten kleinen Prismen ab."

The products that I obtained by Walther's third and fourth method could be made to crystallize at will in the form of needles or prisms. In order to obtain the needle form, a strong ligroïn or petroleum ether is to be taken and this cooled rapidly. If the solutions are dilute or moderately di-

lute, and are slowly cooled, or if allowed to evaporate spontaneously, prisms are invariably obtained. Apparently the prisms are obtained more readily the purer the material. No difference in melting-point was observed between the needles and prisms when these forms were prepared from pure material. The difference in solubility of these forms is only apparent; the prisms are thicker, larger crystals, and therefore, of course, dissolve less *rapidly* than the finely divided slender needles.

Platinum double salts of the supposed new amidines were obtained by Walther in each case, but since these were obtained from impure material, nothing would be gained by examining these. Attention was directed therefore entirely to the amidines.

The formation of only one amidine in reactions III and IV shows that the reaction is not a direct double decomposition, but that it involves an addition and then a separation. For example, both imide chlorides formed from the formyl compounds add the base giving the same compound, *i. e.*, the hydrochloric acid salt of the amidine, and this naturally breaks down in one way, or chiefly in one way:



The above addition-product can separate hydrogen chloride in either of two ways according as the double bond in the free amidine is between the methenyl group and the aniline or the toluidine rest. These reactions, therefore, show nothing in regard to the structure of methenylphenylparatolylamidine.

The Product Obtained by the First Method.

The directions for the preparation of the amidine melting at 120° are somewhat indefinite. Walther states: "Wird Diphenylmethenylamidin mit 1 mol. freien *p*-Toluidins längere zeit erhitzt, so erhält man eine Abscheidung von Anilin. Das resultirende gemischte Amiden bildet shöne weisse Nadeln von Schmelzp. 120°."

No temperatures are given, nor is the solvent stated which was used in the purification (?) of the product. Attempts to prepare this amidine were made as follows: 1.2 grams methenyldiphenylamidine and 0.6 grams of paratoluidine were heated to 100° for about three days. The material on cooling then became a dark-colored semi-solid mass. It was dissolved in cold alcohol and precipitated with water, dried on a plate, and then crystallized from ligroïn. It separated finally in the form of white needles, as Walther states, but the different crystallizations melted about as follows:

I.	102°–110°	IV.	125°–127°	VII.	131°–133°
II.	117°	V.	127°–129°	VIII.	131°–133°
III.	120°–125°	VI.	128°–131°		

In the next experiment a larger quantity of material was taken. 5.5 grams of methenyldiphenylamidine and 3.0 grams of paratoluidine were kept at about 80° for four days and nights. The black mass was then taken up in alcohol precipitated with water, dried, and boiled in ligroïn with animal charcoal. On crystallizing from ligroïn needles separated, and the following melting-points were obtained:

I.	100°–108°	IV.	121°–125°	VII.	135°–136°
II.	112°–115°	V.	125°–129°	VIII.	135°–136°
III.	115°–122°	VI.	130°–132°		

The above results show that the product thus obtained is a mixture, and that the amidine crystallizing in white needles, as described by Walther, is undoubtedly impure methenyldiphenylamidine. The melting-point of this is given by various observers from 135°–140°. Other solvents besides ligroïn were tried but no amidine melting constantly at 120° was obtained. The product was readily soluble in alcohol, ether, carbon disulphide, benzene, and chloroform. It had the appearance and properties of methenyldiphenylamidine.

The Product Obtained by the Second Method.

According to the second method, by heating methenyldiparatolylamidine[1] with aniline hydrochloride for a half hour

[1] In describing methenyldiparatolylamidine as new, Walther overlooks the fact that this amidine was obtained by Senier (Ber. d. chem. Ges., **18**, 2294). Later this amidine and also methenyldimetanitrophenylamidine (dinitrodiphenylformamidine) was described in This JOURNAL, **18**, 517, by Comstock and others.

in alcoholic solution, an amidine melting at 132° should result. The solvent used in purifying is not stated.

An experiment to confirm this statement was undertaken as follows: 2.9 grams of methenyldiparatolylamidine and 1.7 grams of aniline hydrochloride were warmed in a small amount of alcohol for a half hour on the steam-bath. (If warmed for a longer time the amidine is decomposed and nothing separates.) On cooling a mass of needles separated. These were dissolved in alcohol and precipitated with dilute ammonia, dried, and crystallized repeatedly from ligroïn. The products from the successive crystallizations gave approximately the following melting-points:

I. 125°	IV. 133°–137°	VII. 137°–140°
II. 132°	V. 135°–138°	
III. 132°–136°	VI. 137°–140°	

A portion of the hydrochloride was crystallized four times from alcohol and then decomposed with ammonia. Thus obtained it melted at about 135°–136°. When the crude amidine was crystallized twice from absolute alcohol, in which it is quite soluble, it melted from 132°–135°.

In another experiment 5 grams of the amidine and 3 grams of aniline hydrochloride were taken. The hydrochloric acid salt resulting on warming this mixture was crystallized six times from absolute alcohol and then decomposed with dilute ammonia, the dry product melted not sharply at 133°. However, on crystallizing this once from considerable low-boiling ligroïn, it came down in the form of lozenges and flattened bunches of crystals, representing exactly methenyldiparatolylamidine when crystallized under the same conditions. In this form when dry it melted fairly well at 140°.

The above results show that the material obtained by this method, and melting at about 132° is a mixture which, when crystallized, gives methenyldiparatolylamidine.

The Products Obtained by the Third and Fourth Methods.

The third method consists in treating *p*-formtoluide with aniline and phosphorus trichloride. No details are given for the conversion of the reaction-product into the amidine. It is

stated that from petroleum ether the amidine separates in needles melting at 98°.

An experiment according to this method, using the quantities given by Walther, was performed as follows: 5 grams *p*-formtoluide and 3.6 grams of aniline were mixed and treated with an excess of phosphorus trichloride.

A violent reaction took place and the mass solidified. The material was washed with water, taken up in alcohol, and precipitated with dilute ammonia, dried, and crystallized from petroleum ether as directed. It then separated in needles or prisms according to the conditions already stated in the introduction. The material, after one crystallization from petroleum ether, melted from 102°–103°, and showed no signs of melting at 98°. After four crystallizations from ligroïn the material melted from 103°.5–104°.

In another experiment 10 grams of *p*-formtoluide, melting at 52°, and 7.2 grams of freshly distilled aniline were mixed; then phosphorus trichloride was slowly added in excess. The product thus obtained was treated as in the previous experiment. The free amidine was crystallized sixteen times from petroleum ether. It separated in needles and prisms, and the following are some of the melting-points which were observed:

I.	97°.0– 97°.5	IX.	102°.0–102°.5	XIV.	103°.5–104°
III.	98°.0–100°	XI.	102°.5–103°	XV.	103°.5–104°
VI.	100°.5–101°.5	XIII.	103°.0–104°	XVI.	103°.5–104°

In another experiment a specimen of *p*-formtoluide was used which was carefully freed from all traces of *p*-toluidine, and which after several crystallizations from ether melted sharply from 53°–54°. This gave the same result as stated in the first experiment above.

Several attempts were made to prepare this amidine from specimens of crude *p*-formtoluide melting at 52°, and from which *p*-toluidine had not been removed by treating with dilute hydrochloric acid and water. In these cases products were obtained melting at about 85°, and in one of these cases the material was crystallized seven times from ligroïn without raising its melting-point above 86°. On the other hand,

when pure *p*-formtoluide was used, even the crude product melted higher than this. The lowering of the melting-point in these cases is, therefore, due to the presence of *p*-toluidine in the *p*-formtoluide used.

The fact that the amidine prepared by the third method, and from pure materials, melts lower than when prepared by the fourth, is now readily explained as follows: The phosphorus trichloride decomposes a small part of the *p*-formtoluide into *p*-toluidine hydrochloride, and this, by taking part in the reaction, effects a contamination (probably methenyldiparatolylamidine) that is difficult or impossible to remove by repeated crystallizations. On the other hand, the conditions in the fourth method are different. In that case there is no *p*-formtoluide present to form methenyldiparatolylamidine, and, if the formyl compound is decomposed, aniline is separated, this then forms methenyldiphenylamidine, which is more soluble in petroleum ether than the chief product, the mixed amidine. Hence, the material prepared by the fourth method is more readily purified.

An experiment, according to the fourth method, gave the following result: 5 grams of formanilide and 4.8 grams of *p*-toluidine were mixed and treated precisely as in the above experiment. The product from petroleum ether came down in needles or prisms, and after four crystallizations melted from 103°.5–104°.5.

From the above results it is concluded that only one methenylphenylparatolylamidine exists. In conclusion, the author expresses his indebtedness to Mr. J. A. Hall, who has assisted him in the present work.

NEW HAVEN, CONN., March, 1897.

Contributions from the Chemical Laboratory of Case School of Appled Science.

XXV.—INVESTIGATIONS ON AMERICAN PETROLEUM.

ON THE COMPOSITION OF A SOUTH AMERICAN PETROLEUM.[1]

BY CHARLES F. MABERY AND ARTHUR S. KITTELBERGER.

It has long been known that large deposits of petroleum

[1] Presented to the American Academy of Arts and Sciences, October, 1896. Aid in the work described in this paper was given by the Academy from the C. M. Warren Fund for Chemical Research.—C. F. M.

are to be found in various districts in South America, but beyond a limited use of the crude oil in lubrication, until recently no demand has been created for this petroleum. In the Argentine Republic are found heavy oils that deposit paraffin on distillation. In an examination of these oils by Engler and Ottin, hydrocarbons were found of the series $C_n H_{2n+2}$ and $C_n H_{2n}$; they are said to yield a good illuminating oil. The oil fields of Peru and Bolivia have long been known, and large quantities of petroleum products are here obtained. The most promising oil fields hitherto in South America are those of Venezuela, and those deposits are receiving more attention in the preparation of commercial products.

The peculiar character of South American petroleum was brought to the attention of one of us (Mabery) in an examination which he was called upon to make by Mr. Horace M. Wilson, of Cambridge, Mass., who collected a specimen of oil while "prospecting" along the Magdalena River in the United States of Colombia. A few miles from the river, in a rocky section of country, he discovered oil oozing up through a pool of water from a fissure in the rocks below. Oil was also observed escaping in bubbles through the water in a brook, where it formed a beautiful green layer three yards square. These sources and another within a range of two thousand feet were the only ones observed in a distance of fifteen miles. The geological formations in this section consist of sandstones and shales tilted in nearly a horizontal position. At a distance of forty miles was a very large deposit of asphalt, hard and brittle like coal. About eighty gallons of this oil was collected at a rate of five gallons in twenty-four hours, of which the larger portion mixed with lard oil was used as a lubricator on car axles, for which it was found to be well adapted. Mr. Wilson brought home fifteen gallons of the oil, which was placed at our disposal for this examination.

The specific gravity of the crude oil was found to be 0.9480 at 20°. It is a high sulphur oil, as shown by the following determinations: (I), 0.70; (II), 0.66 per cent. It absorbed bromine equivalent to 12.09 per cent. It also contains a large

quantity of nitrogen, as shown by the following determinations: (I), 0.321; (II), 0.315 per cent. A determination of ash in the crude oil was made, in which 29.1360 grams of the oil was burned, and the ash ignited until all carbon was consumed. The residue weighed 0.313 gram, equivalent to 0.011 per cent., or the same amount of ash as is obtained from Ohio crude oil.[1] The ash contains much iron, as shown by its brown color.

Determinations of carbon and hydrogen in the crude oil gave the following results:

	I.	II.
C	85.80	85.45
H	12.02	11.79

The crude oil was dark in color, thick and viscous, flowing very slowly at ordinary temperatures. In attempting to distil it under ordinary atmospheric pressure, nothing came over below 260°, and between this point and 345° it distilled in the following proportions, beginning with 290 cc.

	—310° 70 cc.	310°-345° 70 cc.
Specific gravity	0.8749	0.8615
Bromine-absorption	0.46	34.96

As the great increase in bromine-absorption shows, the distillate 310°–345° was badly cracked, and it had the very disagreeable odor of the worst decomposition-products of high petroleum distillates. The lower fraction had only the natural odor of an undecomposed distillate. Nothing could be distilled above 345°, and the residue was completely coked. In respect to the instability of its least volatile portions, this oil differs from any North American oil that has come under my observation (Mabery). It was therefore evident that another method of distillation must be resorted to with any hope of separating without decomposition the principal constituents.

In subjecting the crude oil to distillation *in vacuo* under 50 mm., the first distillate came over at 100°, and below 250° the following weights were collected from 14.5 kilos, after the fourth distillation. It cannot be assumed that the absence of

[1] Proc. Amer. Acad., 31, 20.

more volatile constituents was the result of evaporation by exposure on the surface of the water where the oil was found, since it was collected as soon as it appeared. No doubt such volatile portions as constitute gasoline on long exposure under such circumstances would be lost, but no constituents, such as higher members of $C_n H_{2n+2}$, which do not appear in this oil.

	—130°	130°-135°	135°-140°	140°-150°	150°-155°	155°-160°	160°-165°
Grams	265	100	115	225	200	65	95
Sp. gr.					0.8706	0.8736	0.8747

	165°-170°	170°-175	175°-180°	180°-185°	185°-190°	190°-195°
Grams	130	130	70	125	115	155
Sp. gr.	0.8784	0.8806	0.8846	0.8858	0.8867	0.8884

	195°-200°	200°-205°	205°-210°	210°-215°	215°-220°	220°-225°
Grams	140	165	95	110	100	145
Sp. gr.	0.8926	0.8947	0.8964	0.8989	0.9020	0.9045

	225°-230°	230°-235°	235°-240°	240°-245°	245°-250°	+250°
Grams	145	150	100	93	75	130
Sp. gr.	0.9078	0.9113	0.9137			

Distillation of the fractions below 150° amounting to 700 grams was continued under atmospheric pressure, collecting within the limits of two degrees. After five distillations, ten in all from the beginning, heaps collected at 170°, 190°, and 212°, although in small quantities. The distillation could not be pushed too far on account of decomposition. The fraction 170°–172° (730 mm.) gave the following percentages of carbon and hydrogen:

0.1456 gram of the oil gave 0.4556 gram CO_2, and 0.1864 gram H_2O.

	Calculated for $C_{10}H_{20}$.	Found.
C	85.71	85.33
H	14.29	14.23

Unfortunately there was not enough of this fraction to determine its specific gravity. A determination of sulphur gave 0.05 per cent. Its bromine-absorption was found to be 3.5 per cent. No other heap appeared in the distillates below 190°. At 190°–192° more collected, evidently corresponding to a hydrocarbon boiling at 196°. A determination of the specific gravity of this distillate gave 0.8381. It absorbed

bromine amounting to 3.56 per cent. A determination of sulphur gave 0.10 per cent. A combustion gave the following percentages of carbon and hydrogen:

I. 0.1696 gram of the oil gave 0.5332 gram CO_2. The water was lost.

II. 0.1542 gram of the oil gave 0.4846 gram CO_2, and 0.1912 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found. I.	II.
C	85.71	85.73	85.69
H	14.29	....	13.78

The distillate was treated with a mixture of nitric and sulphuric acids, then with fuming sulphuric acid. In the first treatment, a very small quantity of a nitro compound separated as an oil, showing a trace of an aromatic hydrocarbon. The fuming acid produced no appreciable action.

A determination of carbon and hydrogen in this product gave the following results:

0.1618 gram of the oil gave 0.5019 gram CO_2, and 0.2087 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	85.47
H	14.29	14.33

A determination of the specific gravity of the oil after this treatment gave 0.8333. Besides a very small proportion of aromatic hydrocarbon $C_n H_{2n-6}$, evidently this distillate is composed of a single body, although analysis alone is not sufficient to determine whether its composition is represented by the formula $C_{11}H_{22}$ or $C_{12}H_{24}$.

Above 192° no distillates collected in appreciable amounts below 210°. At 212°–214° a larger quantity collected, evidently corresponding to a hydrocarbon boiling at 216°, which has been found in other oils. A determination of its specific gravity gave 0.8483. It absorbed bromine equivalent to 4.29 per cent., and contained 0.04 per cent. of sulphur. A determination of the carbon and hydrogen gave the following percentages:

0.1555 gram of the oil gave 0.4887 gram CO_2, and 0.1992 gram H_2O.

	Calculated for $C_{12}H_{24}$.	Found.
C	85.71	85.72
H	14.29	14.23

A small quantity of nitro product was formed, when this distillate was treated with nitric and sulphuric acids, and fuming sulphuric acid then removed more of the nitro compound from the oil. The oil shaken with sodic hydrate imparted a yellow color to the alkaline solution ; it was then redistilled for analysis :

0.1590 gram of the oil gave 0.4984 gram CO_2, and 0.2037 gram H_2O.

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	85.48
H	14.29	14.23

A determination of the specific gravity of the oil after treatment with acids gave 0.8484, the same value as was obtained for the crude distillate. It was therefore evident that this petroleum consists mainly of a single series of hydrocarbons, with a mere trace of aromatic hydrocarbons $C_n H_{2n-6}$. What this series is does not appear from these results, at least so far as its relation to the series of hydrocarbons hitherto discovered in petroleum. In the proportions of carbon and hydrogen, the series $C_n H_{2n}$, is indicated. Neither the crude oil nor any of these distillates deposit paraffin, even at low temperatures. The higher distillates are thick and viscous, light yellow in color, and unquestionably are undecomposed constituents of the crude oil.

With nitric and sulphuric acids the constituents described in this paper are as slightly affected as are the naphtenes in the Russian oil. This fact, together with the results of analysis corresponding to the series $C_n H_{2n}$, and the high specific gravity, point to a similar composition for these bodies, and the small proportion of the crude oil distilling below 220° seems, therefore, to be composed almost exclusively of naphtenes, which is the first instance of an American petroleum having been found containing these hydrocarbons in any considerable quantity. The higher distillates from this petroleum will receive further attention in connection with the corresponding portions of other American oils.

Having at hand a specimen of petroleum from Oregon, resembling the heavier California products, with a specific gravity nearly the same as that of the South American oil described above, it seemed of sufficient interest to submit it to an examination in connection with that of the South American oil. The crude oil was very thick and dark, with a specific gravity of 0.9597 at 20°. Like the California oils, as shown by Peckham, it contains a large percentage of nitrogen compounds. A Kjeldahl determination gave 0.868 per cent. of nitrogen. This is also a high sulphur oil, as shown by a combustion which gave 1.19 per cent. of sulphur. It is also a high carbon oil; a combustion gave 86.06 per cent. of carbon, and 11.87 per cent of hydrogen. A very small proportion distils under atmospheric pressure, without decomposition; even under diminished pressure, the amounts distilling below 250° are small.

In attempting to separate the constituents of this oil from the distillate first collected *in vacuo*, the portions below 250°, about the same in amount as the corresponding distillates from the South American oil, were carried through ten distillations under atmospheric pressure, which brought together larger quantities at 169°–170°, 190°–191°, and 212°–214°. The portions collected at 85°–150° in the first distillation gave as its specific gravity at 20°, 0.8755; the distillate 150°–225°, 0.9038; and the distillate 225°–250°, 0.9271. After the tenth distillation, the fraction 170°–171° gave as its specific gravity, 0.8200; the fraction 189°–190°, 0.8330; and the fraction 212°–214°, 0.853. A combustion of the fraction 189°–190° gave the foilowing percentages of carbon and hydrogen:

0.1510 gram of the oil gave 0.4757 gram CO_2, and 0.1835 gram H_2O.

C	85.90
H	13.51

After purification with nitric and sulphuric acids, the composition of this oil was not essentially changed:

0.1484 gram of the oil gave 0.4643 gram CO_2, and 0.1839 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.33
H	14.29	13.77

The fraction 212°-214°, without purification, gave the following results:

0.1457 gram of the oil gave 0.4625 gram CO_2, and 0.1757 gram H_2O.

C	86.46
H	13.40

By treatment with a mixture of nitric and sulphuric acids, and then with fuming sulphuric acid, this distillate was only slightly affected:

0.1343 gram of the oil gave 0.4231 gram CO_2, and 0.1677 gram H_2O.

	Calculated for C_nH_{2n}.	Found.
C	85.71	85.90
H	14.29	13.88

Unfortunately the quantities of these distillates were too limited to permit of further examination. The principal object, however,—to ascertain whether any members of the series C_nH_{2n+2} were present at all, or the aromatic hydrocarbons C_nH_{2n-6} in more than minute proportions,—was attained. Evidently the main body of this oil is composed of a series with less hydrogen than the former and more than the latter. The oil distils in such small quantities, even *in vacuo*, below 220°, that it will be interesting to ascertain the composition of the distillates above this point.

Contributions from the Chemical Laboratory of the Lehigh University.

IV.—THE ACTION OF CERTAIN ALCOHOLS ON *ASYM*-METADIAZOXYLENESULPHONIC ACID.

By W. B. Shober and H. E. Kiefer.[1]

The starting-point in this investigation was the preparation of *a*-metaxylidinesulphonic acid. The directions given by Jacobson and Ledderboge[2] were followed. A mixture of 300 cc. of *a*-metaxylidine (Kahlbaum's preparation), boiling at

[1] Dissertation submitted to the Faculty of the Lehigh University, for the Degree of Doctor of Philosophy by Herman Eugene Kiefer, June, 1896.

[2] Ber. d. chem. Ges., 16, 193.

211°–212°, 150 cc. concentrated sulphuric acid, and 300 cc. of fuming sulphuric acid, was heated in a sulphuric-acid bath for three hours at a temperature of 140°–150°. On cooling the reaction-mixture solidified; it was slightly warmed and poured into 4 liters of ice-water. The sulphonic acid separating out was filtered off with the aid of suction; the pasty mass was then kneaded with an excess of barium carbonate, boiled with water and filtered while hot through muslin. The filtrate was treated with a sufficient amount of potassium carbonate to precipitate the barium, filtered and evaporated to crystallization. The potassium salt was obtained in good crystals of a light yellow color.

Diazotization of the Potassium Salt.

The directions given by Sartig[1]—diazotization with potassium nitrite in hydrochloric-acid solution—were followed exactly, but satisfactory results could not be obtained; another method was therefore tried. The potassium salt obtained, as above described, was converted into the free acid by treatment with hydrochloric acid. The free acid was washed on the filter with much cold water and dried on porous plates.

Ten grams of the dry xylidinesulphonic acid was converted into a thick paste with water, and nitrous fumes, from arsenic trioxide and nitric acid, were passed into it until the mass dissolved; this occurred in fifteen minutes. Four volumes of cooled alcohol was then added and the mixture allowed to stand fifteen minutes in an ice-salt mixture. The diazo compound was filtered off, washed with alcohol, then ether, and dried in the air on filter-paper; the dried compound weighed 9 grams. It was afterwards boiled with absolute alcohol under pressure; the decomposition was complete, there being no residue, thus showing that the diazo compound was not contaminated with any xylidinesulphonic acid which had escaped diazotization.

The theoretical yield of the diazo compound from 10 grams of the amido acid is 10.6 grams. We obtained 9 grams, or 94 per cent. of the theoretical.

[1] Ann. Chem. (Liebig), **230**, 337.

Action of Methyl Alcohol on a-Metadiazoxylenesulphonic Acid at the Atmospheric Pressure.

The diazo compound was made by the method just described. The methyl alcohol used in this and the following experiments was Kahlbaum's purest preparation. It was allowed to stand over chemically pure lime several weeks before it was used. The two substances were placed in a flask, to which a reflux-condenser was attached, and heated on a water-bath. Decomposition began almost immediately, resulting in the formation of a dark, yellowish liquid. The excess of alcohol was distilled off, the resulting oily residue diluted with water, and neutralized with barium carbonate. The barium salt was converted into the potassium salt, this into the sulphon chloride and finally into the amide. An attempt was made to crystallize the amide from water, but it was unsuccessful, owing to the great insolubility of the compound; the proper solvent is alcohol. The amide was boiled with animal charcoal in alcohol and recrystallized several times. Two compounds were found, one melting at 136°, which is the xylenesulphonamide; another, melting at 190°, which, as shown by the analysis given below, is the amide of methoxyxylenesulphonic acid. The latter compound was formed in much larger quantity.

Action of Methyl Alcohol on the Diazo Compound at a Pressure of 400 mm. of Mercury.

The substances were placed in a pressure-flask, to which was attached a manometer. Upon applying heat, the reaction began almost immediately and was completed in thirty minutes. The alcohol was distilled off, and from the oily residue crystals of the free acid separated out on standing. These were dissolved by adding water; the acid liquid was neutralized with barium carbonate. The barium salt was converted into the potassium salt from which the chloride and amide were prepared. Two amides were again found; one melting at 190° and the other at 137°. The quantity of the latter was very small.

Action of Ethyl Alcohol on the Diazo Compound at Atmospheric Pressure.

Sartig[1] treated the diazo compound obtained by diazotizing the potassium salt in acid solution, with alcohol at the ordinary pressure. He found that the alcohol dissolved the diazo compound, but states that no decomposition took place on boiling. Our results are at variance with this statement.

The diazo compound and absolute alcohol were placed in a flask, to which a reflux-condenser was attached. The experiment was carried out in the same manner as the preceding ones. Two amides were formed as before, one melting at 137° and the other at 169°. The hydrogen amide (melting-point 137°) was formed in smaller quantity than the other.

In order to be certain of the identity of the amide melting at 169°, a sulphur determination was made with the following result:

0.2412 of amide gave 0.2453 gram of barium sulphate (Carius' method) corresponding to 13.98 per cent. of sulphur. The theory for sulphur in ethoxyxylenesulphonamide requires 13.99 per cent. This result, taken in connection with the melting-point, 169°, was deemed sufficient to characterize the compound. Moody[2] gives the melting-point 169°–170°.

Action of Ethyl Alcohol on the Diazo Compound at a Pressure of 360–380 mm. of Mercury.

The compounds were placed in the pressure-flask and heat applied. Reaction began at once and was complete after thirty-five minutes. The reaction-product was treated as in the preceding experiments. Two amides were again found; the quantity of the hydrogen amide was very small.

—Sartig[3] treated the diazo compound with absolute alcohol at a pressure of 360 mm. of mercury. He says: "The diazo compound decomposes on heating with absolute alcohol under a pressure of 360 mm. of mercury, but not with the formation of xylenesulphonic acid, but of ethoxyxylenesulphonic acid."

Since the hydrogen compound—xylenesulphonic acid—is formed in such small quantity, it is probable that Sartig

[1] Ann. Chem. (Liebig), **230**, 337. [2] Proc. Chem. Soc., 1891, 189.
[3] *Loc. cit.*

overlooked its presence. He prepared, analyzed and described the barium salt, $(C_6H_2.CH_3.CH_3.OC_2H_5.SO_3)_2Ba+3H_2O$. It crystallizes in white microscopic leaflets, moderately soluble in water and in alcohol.

We prepared the potassium salt which crystallizes in leaflets; it is easily soluble in water, more difficultly soluble in alcohol. Its composition was not determined.

Moody[1] obtained the same ethoxyxylenesulphonic acid by boiling the diazo compound with "dehydrated methylated spirit." This result does not agree with that obtained by Sartig. Since Moody makes no reference to pressure, it is assumed that he effected the decomposition at the ordinary pressure. Sartig, working under the same conditions except that he used absolute alcohol, found that no decomposition took place. Judging from Moody's experiments, our own and others on record, it is probable that Sartig's observation is incorrect. It is possible, however, that the diazo compound may be more susceptible to the action of methylated spirit than to that of absolute alcohol.

Action of Ethyl Alcohol on the Diazo Compound at a Pressure of 900 mm. of Mercury.

The experiment was conducted in the usual manner: 4.2 grams of the diazo compound and 100 cc. of absolute alcohol were placed in the pressure-flask and heated. The decomposition was complete in a short time. The reaction-product was treated as before. Two amides were found; one melting at 160°, the ethoxyamide, and the other at 137°. The latter was formed in minute quantity.

Action of Propyl Alcohol on the Diazo Compound at a Pressure of 820–840 mm. of Mercury.

The propyl alcohol used was Kahlbaum's preparation (boiling-point 96°). It was dehydrated over lime. A mixture of 4.3 grams of the diazo compound and 100 cc. of propyl alcohol was treated in the usual way. The decomposition was complete in thirty minutes. Two amides were formed: one melting at 137°; the other at 145°. This latter was formed

[1] Proc. Chem. Soc., 1891, 189.

in great excess. As shown by the analysis given below, it was propoxyxylenesulphonamide.

A Study of the Asym-metamethoxyxylenesulphonic Acid and Some of its Derivatives.

The barium salt obtained by decomposing *a*-metadiazoxylenesulphonic acid with methyl alcohol and neutralizing the reaction-product with barium carbonate, was divided into two portions. One portion was converted into the corresponding amide. An analysis (given below) proved it to be the amide of methoxyxylenesulphonic acid. The other portion was dissolved in water and treated with just enough sulphuric acid to precipitate all the barium; the barium sulphate was filtered off and the filtrate concentrated. On standing, the free methoxyxylenesulphonic acid separated out in a mass of brownish needles. By boiling with animal charcoal and recrystallizing several times from water, the crystals were obtained free from color.

The acid decomposes on heating; it is very soluble in water, alcohol, and ether; difficultly soluble in pure benzene, from which it crystallizes in microscopic needles.

Potassium Salt, $C_6H_3.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}H_3.\overset{6}{S}O_3K + \frac{1}{2}H_2O$. — This salt was made by treating the barium salt with potassium carbonate, filtering off the barium carbonate, and concentrating the filtrate to crystallization. An analysis for potassium and water gave the following results:

0.08495 gram of the substance heated to 160° for one hour lost 0.00315 gram.

0.08495 gram of the substance gave 0.028 gram of potassium sulphate.

	Calculated for $C_9H_{11}SO_4K + \frac{1}{2}H_2O$.	Found.
K	14.79	14.86
$\frac{1}{2}H_2O$	3.41	3.70

The potassium salt is extremely soluble in water, readily soluble in dilute alcohol, more difficultly soluble in ordinary alcohol. From a concentrated water solution it crystallizes in very fine, yellow needles; from dilute alcohol in larger needles.

Barium Salt, $(C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.\overset{4}{O}CH_3.\overset{6}{S}O_3)_2Ba + 4H_2O$.—This salt was obtained by treating the free acid with an excess of barium carbonate, filtering off the excess, and evaporating to crystallization.

An analysis for barium and water gave the following results:

0.1709 gram of the salt was heated for one and a half hours at 150°; the loss in weight was 0.0191 gram.

0.1709 gram of the salt gave 0.0615 gram of barium sulphate.

	Calculated for $C_{18}H_{22}S_2O_6Ba + 4H_2O$.	Found.
Ba	21.46	21.17
$4H_2O$	11.25	11.18

The salt is readily soluble in water, from which it crystallizes in yellow, warty masses or in clusters of ill-defined needles; it is more difficultly soluble in 80-per cent. alcohol. From the alcoholic solution it crystallizes in small lustrous, yellow plates.

Copper Salt, $(C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.\overset{4}{O}CH_3.\overset{6}{S}O_3)_2Cu + 4H_2O$.—This compound was prepared by adding copper sulphate to a solution of the barium salt. A determination of the water of crystallization gave the following result:

0.47952 gram of the salt lost 0.0597 gram on being heated for two hours at 160°.

	Calculated for $C_{18}H_{22}S_2O_6Cu + 4H_2O$.	Found.
$4H_2O$	12.73	12.45

The hydrous crystals are apple-green in color; on being dehydrated they become yellow. The salt is soluble in water, less soluble in alcohol; from alcohol it crystallizes in fine needles.

A *Zinc* and a *Sodium Salt* were also prepared. Both are easily soluble in water and less soluble in alcohol. They were not analyzed.

The Amide, $C_6H_2.\overset{1}{C}H_3.\overset{3}{C}H_3.\overset{4}{O}CH_3.\overset{6}{S}O_2NH_2$.—This compound was prepared in the usual way from the potassium salt. An analysis gave the following results:

0.2283 gram of the substance gave 0.4216 gram of carbon dioxide.

0.2493 gram of the substance gave 0.1321 gram of water.

0.2057 gram of the substance gave 0.22673 gram of barium sulphate, Carius' method.

0.8735 gram of the substance gave 0.06615 gram of ammonia (Kjeldahl-Gunning Method).

	Calculated for $C_9H_{13}SNO_3$.		Found. I.	II.
C_9	107.73	50.20	50.36	...
H_{13}	13.00	6.05	....	5.90
S	31.98	14.90	15.14	...
N	14.01	6.52	6.23	...
O_3	47.88	....	....	...
	214.60	100.00		

The amide is insoluble in cold water, very difficultly soluble in hot water, soluble in alcohol. From its water solution it crystallizes in very fine, white needles; from an alcoholic solution in coarser needles. Several determinations gave 190° as the melting-point.

A Study of Asym-Propoxyxylenesulphonic Acid and Some of Its Derivatives.

The free acid was obtained as follows: Asym-metadiazoxylenesulphonic acid was decomposed in the presence of anhydrous propyl alcohol at a pressure of 850-900 of mm. of mercury. The resulting brownish-red liquid was heated until the alcohol distilled off; then diluted with water, and neutralized with barium carbonate. The excess of barium carbonate and the barium sulphate were filtered off, the filtrate was boiled with animal charcoal, filtered, and evaporated. On standing, crystals of the barium salt were deposited; these crystals were dissolved in water and the solution was treated with a quantity of sulphuric acid sufficient to precipitate all the barium. The barium sulphate was filtered off, and the filtrate evaporated to crystallization. Large tablets, apparently orthorhombic, were deposited.

The acid is very soluble in water and in alcohol. From the alcoholic solution it crystallizes in fine needles. The acid

itself was not analyzed, but an analysis of the amide derived from it is given below.

Barium Salt, $(C_6H_3.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}_6H_2.\overset{6}{S}O_3)_2Ba + 3H_2O$.—The barium salt was prepared by neutralizing the free acid with chemically pure barium carbonate. The excess of barium carbonate was filtered off and the filtrate evaporated to crystallization.

Determinations of barium and water gave the following results:

0.30805 gram of the substance dried in the air for twenty-four hours and then heated to 150° for one hour, lost 0.02385 gram and gave 0.1042 gram of barium sulphate.

0.1746 gram of the substance under the same conditions lost 0.0132 gram and gave 0.0595 gram of barium sulphate.

	Calculated for $C_{22}H_{30}S_2O_8Ba + 3H_2O$.	Found. I.	II.
Ba	20.25	19.89	20.04
$3H_2O$	7.97	7.74	7.56

The barium salt is moderately soluble in water and in alcohol. From the water solution it crystallizes in clusters of small, glistening needles, faintly yellow; from the alcoholic solution clusters of small plates are deposited.

Potassium Salt, $C_6H_3.CH_3.CH_3.OC_6H_2.SO_3K + H_2O$.—The potassium salt was prepared by treating the barium salt with potassium carbonate, filtering off the barium carbonate, and evaporating the filtrate to crystallization. The crystals were dried in the air; a determination for potassium and water gave the following results:

0.24838 gram of the salt heated at 120° for three hours lost 0.01533 gram and gave 0.0728 gram of potassium sulphate.

	Calculated for $C_{11}H_{13}SO_4K + H_2O$.	Found.
K	13.32	13.15
H_2O	5.99	6.17

The salt is easily soluble in water and alcohol. It crystallizes in small yellow needles or in quadratic tablets.

Zinc Salt, $(C_6H_3.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}_6H_2.\overset{6}{S}O_3)_2Zn + 5H_2O$.—This salt was prepared from the barium salt by treating it with

zinc sulphate; the barium sulphate was filtered off and the filtrate evaporated to crystallization. The crystals were dried in the air for twelve hours and over sulphuric acid for twelve hours. A partial analysis gave the following results:

0.19007 gram of the substance on heating to 150° for one hour lost 0.02605 gram and gave 0.04567 gram of zinc sulphate:

	Calculated for $C_{22}H_{30}S_2O_8Zn + 5H_2O$.	Found.
Zn	10.18	9.72
$5H_2O$	14.03	13.70

The salt is very soluble in water, less soluble in alcohol. It crystallizes in fine transparent leaflets or in columns of a slightly yellow color.

The Amide, $C_6H_3.\overset{1}{C}H_3.\overset{3}{C}H_3.O\overset{4}{C}_3H_3.\overset{6}{S}O_2NH_2$.—This compound was prepared from the potassium salt in the usual way: An analysis of it gave the following results:

0.09889 gram of the substance gave 0.1956 gram of carbon dioxide and 0.0667 gram of water.

0.2064 gram of the substance 0.1987 gram of barium sulphate (Carius' method).

	Calculated for $C_{11}H_{17}SO_3N$.		Found.
C_{11}	131.67	54.29	53.93
H_{17}	17.00	7.01	7.47
N	14.01	....	....
S	31.98	13.18	13.22
O_3	47.88	....	....
	242.54		

The amide is very difficultly soluble in water, easily soluble in alcohol. It crystallizes in fine needles, melting at 146°.

Oxidation of Asym-Metamethoxyxylenesulphonamide.

In view of the many interesting results obtained by Remsen and other investigators on oxidizing aromatic sulphonamides, it was deemed advisable to study the behavior of *a*-metamethoxyxylenesulphonamide on oxidation.

In order to obtain a sufficient quantity of the amide, successive quantities of the diazo compound were decomposed with methyl alcohol at a pressure of 800–900 mm. of mercury,

and the reaction-product treated as described above. A different method of diazotization was employed, however. While the method described above usually gave good results, at times due to a slight variation in temperature or in the rapidity of the current of nitrous fumes, the entire quantity of the diazo-compound would decompose. We, therefore, tried another method. The dry metaxylidinesulphonic acid was ground to a very fine powder and suspended in ordinary alcohol, into which cooled nitrous fumes were passed until the substance became granular; the vessel containing the alcohol was surrounded by an ice-salt mixture. By this method we were enabled to convert 100 grams of the amido acid into the diazo compound in three hours; it has the disadvantage, however, that at times a small portion of the acid escapes diazotization.

Ten grams of asym-metamethoxyxylenesulphonamide was ground to a fine powder and triturated with water until a paste was formed: this was transferred to a 2-liter flask containing 1.5 liters of water and 40 grams potassium permanganate. The flask was placed *in* a water-bath, the temperature of which was maintained at 90°–96° for twenty hours. At the expiration of this time the flask was removed, a few drops of alcohol added, and allowed to stand until the manganese compounds had settled. The clear colorless solution was decanted and filtered; the residue was washed with hot water and filtered. The filtrates were poured together, evaporated to one-fourth their volume, and allowed to stand twelve hours, in order that any unoxidized amide might crystallize out. In every experiment a small quantity of the amide was found unoxidized. This was filtered off and an excess of hydrochloric acid added to the filtrate, which was then allowed to stand twelve hours. Long, acicular, white crystals, melting with decomposition at 236°–238°, separated out; these were filtered off, the filtrate concentrated and again allowed to stand for twelve hours. Two kinds of crystals were deposited—those just mentioned and flat, white, flaky crystals melting at 270°–275° with decomposition; they were separated by fractional crystallization.

An analysis of the compound melting at 236°–238° gave the following results:

0.6582 gram of the substance heated for twenty-two hours at a temperature of 120°–140° lost 0.0435.

1.2256 grams of the substance heated for thirteen hours at 150°–160° lost 0.084 gram.

0.2325 gram of the dried substance gave 0.3743 gram carbon dioxide and 0.0962 gram of water.

0.4106 gram of the substance gave 0.022911 gram of nitrogen.

0.4272 gram of substance gave 0.023936 gram of nitrogen (Kjeldahl-Gunning method).

0.2211 gram of the substance gave 0.2083 gram of barium sulphate (Carius' method).

	Calculated for $C_6H_3.CH_3.COOH.OCH_3.SO_2NH_2 + H_2O$.		Found.	
C_9	107.73	44.05	43.91	
H_{11}	11.00	4.49	4.59	
O_5	79.80	....	....	
S	31.98	13.08	12.94	
N	14.01	5.72	5.58	5.60
	244.52	100.00		
H_2O	17.96	6.84	6.61	6.84
	262.48			

The compound, therefore, appears to be methoxysulphaminetoluic acid containing one molecule of water; the carboxyl is probably in the meta position to the sulphamine group. The substance crystallizes in fine needles; it is difficultly soluble in water and ether, more easily soluble in alcohol (melting-point 236°–238°).

Barium Salt, $(C_6H_3.CH_3.OCH_3.SO_2NH_2COO)_2Ba + 7H_2O$. —This salt was prepared by boiling the free acid with chemically pure barium carbonate; the excess of the latter was filtered off and the filtrate evaporated. Attempts to obtain well-formed crystals from the water solution were unsuccessful. From a 50-per cent. alcohol flat, tabular crystals were obtained, a partial analysis of which gave the following results:

0.3723 gram of the substance dried in the air for one and a half hours lost 0.061 gram on being heated to 110° for three hours.

0.3205 gram of the dried salt gave 0.1199 gram of barium sulphate.

	Calculated for $C_{18}H_{22}S_2N_2O_{10}Ba + 7H_2O$.	Found.
Ba	21.93	22.04
$7H_2O$	16.76	16.38

Calcium Salt, $(C_8H_{11}.CH_2.OCH_2.SO_2NH_2.COO)_2Ca + 7H_2O$. —This salt was prepared by boiling the free acid with chemically pure calcium carbonate; the excess of carbonate was filtered off and the filtrate evaporated. As was the case with the barium salt, we were unable to obtain good crystals from the water solution. From 50-per cent. alcohol, flat tabular crystals were deposited. A partial analysis gave the following results:

	Calculated for $C_{18}H_{22}S_2N_2O_{10}Ca + 7H_2O$.	Found.
Ca	7.59	7.70
H_2O	19.60	19.53

A *sodium salt* and a *potassium salt* were also prepared; they are exceedingly soluble in water from which they do not crystallize well. They were not analyzed. The substance melting at 270°–275° contains no nitrogen. Two determinations for carbon gave, respectively, 34.159, and 34.16 per cent.

South Bethlehem, Penna.,
June, 1896.

THE ACTION OF ETHYLIC OXALATE ON CAMPHOR. (II.)

By J. Bishop Tingle.

Introduction.

It has been shown by Claisen and his students[1] that under the influence of sodium ethylate, ketones of the formula $R.CO.CH_3$ or $R.CO.CH_2R$ condense with ethylic oxalate and similar compounds, forming ethereal salts of 1,3-diketo acids —thus acetone and ethylic oxalate yield ethylic acetone oxalate, $CH_3.CO.CH_2.CO.CO.OC_2H_5$. Ketones of the formula

[1] Ann. Chem. (Liebig), **281**, 306.

$R.CO.CHR_2$ do not react in this manner, and W. Wislicenus found[1] that the corresponding acids $R_2.CH.CO.OC_2H_5$ also fail to replace the hydrogen of the methine group by acid radicles. At the time this work was commenced, in 1889, camphor was usually represented by Kekule's expression,

$$C_8H_{14}.CH\begin{matrix}\diagup CH_2.CO \diagdown \\ \diagdown CH_2.CH \diagup\end{matrix}C.CH_3,$$

the position of the double bond and also of the carbonyl group being stated by himself as somewhat doubtful. The attempt was therefore made to condense camphor and ethylic oxalate, and the resulting product, ethylic camphoroxalate,

$$C_8H_{14}\begin{matrix}\diagup CH.CO.CO.OC_2H_5 \\ \diagdown CO\end{matrix}$$

was, together with some of its derivatives, briefly described in 1890.[2] Circumstances compelled the work to be suspended, and it has only recently been found possible to prosecute it further. During the past few years the constitution of camphor has received much attention from various chemists, including Von Baeyer, W. A. Noyes, Tiemann, and Collie; the formulæ for this substance that have perhaps attracted most notice being those of Bredt, Tiemann, and Collie,[3] but as these all recognize the presence in the molecule of the —CH_2.CO— group, this part of the work has lost in interest. On the other hand, a controversy has sprung up between Nef, Claisen, and others, as to the constitution of the 1,3-diketones and keto-acids; tthe latter[4] regards them as essentially true diketones, except possibly where two isomeric forms of the same compound are known, whilst the former[5] considers that he has proved them to be unsaturated hydroxy derivatives with a constitution corresponding with that first suggested by Geuther for ethylic acetoacetate; *viz.*, CH_2.C.OH : CH.CO.OC_2H_5. The compounds chiefly investigated from this point of view, both by Claisen and Nef, all contain strongly negative groups, such as CH_3.CO and C_6H_5CO; the radicle—$CO.OC_2H_5$—is comparatively feeble in this respect,

[1] Am. Chem. (Liebig), **246**, 329 and 339. [2] J. Chem. Soc., **57** (1890), 652.
[3] Comp. W. A. Noyes: This JOURNAL, **18**, 1. [4] Ann. Chem. (Liebig), **277**, 162.
[5] *Ibid*, **266**, 52; **276**, 200; **277**, 59.

as Bishop, Claisen, and Sinclair have shown.[1] Since the camphyl radicle is also but very feebly negative, and has a relatively great mass (= 151), it appeared possible that the further study of ethylic camphoroxalate might throw light on the constitution of this class of bodies, and the work has therefore been recently resumed. At present the results hardly warrant any strong assertions for or against either constitution, but it appears desirable to place on record the work already done, so as to reserve the field for further study.

Theoretical.

The formation of ethylic camphoroxalate occurs most readily under the influence of sodium, the sodium camphor acting like sodium ethylate; according to Claison's view[2] the reaction occurs in two stages:

(1) $C_{10}H_{15}ONa + C_2H_5O.CO.CO.OC_2H_5 =$

$$C_2H_5O.CO.C(ONa)(OC_{10}H_{15}).OC_2H_5.$$

(2) $C_2H_5O.CO.C(ONa)(OC_{10}H_{15}).OC_2H_5 + H_2C(CO)C_8H_{14} =$

$$C_2H_5O.CO.CONa : C(CO)C_8H_{14} + C_{10}H_{16}O + C_2H_5OH,$$

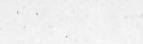
the sodium salt when acidified yielding the free ketone

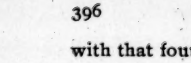
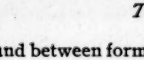
$$C_8H_{14}(CH.CO.CO.OC_2H_5)CO.$$

The hydrogen, liberated during the formation of sodium camphor, reduces a portion of the free camphor to borneol.

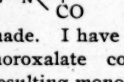
Ethylic camphoroxalate offers a rather remarkable contrast to formylcamphor, the latter, as Claison, Bishop, and Sinclair have shown (*loc. cit.*), is a very strong acid and readily forms an anhydride, etc., but the former does not appear to form a copper salt; it is quickly decomposed when heated, and in presence of alkali is rapidly hydrolyzed, giving camphoroxalic acid. This difference in behavior is somewhat analogous

[1] Ann. Chem. (Liebig), **281**, 319. [2] *Loc. cit.*

with that found between formyl camphor and ethylic camphorcarboxylate,  , to which reference has already been made. I have previously shown (*loc. cit.*) that ethylic camphoroxalate combines with phenylhydrazine, although the resulting monohydrazone or hydrazide,

 or 

was not obtained in a state of complete purity. This compound, under the conditions described below, loses the elements of water and forms ethylic camphylphenylpyrazolecarboxylate

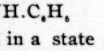


which, when hydrolyzed, yields the free acid.

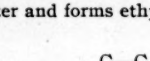
Camphoroxalic acid, $C_{12}H_{16}O_4$, I had also prepared before. It is extremely stable towards alkali, and may be boiled for several hours with concentrated aqueous alcoholic potash or soda, without undergoing decomposition. With hydroxylamine, at the ordinary temperature, in presence of sodium hydrogen carbonate, it yields an additive compound,

$$C_{12}H_{16}O_4.NH_2O.$$

The formation of this tells in favor of the formula

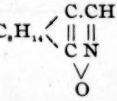


for the acid, since it is scarcely to be expected that hydroxylamine would yield a stable compound of such a nature with a substance containing two carbonyl groups. In accordance with this, the formula of the additive compound is

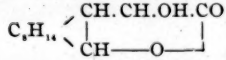
 ,

the alternative formula

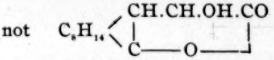
being eliminated by the production of camphylisoxazole



which Bishop, Claisen, and Sinclair were unable to prepare from sodium formylcamphor and hydroxylamine hydrochloride (*loc. cit.*). The production of a γ-lactone

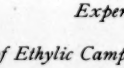


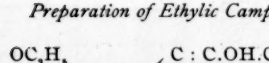
(not



as given in my first paper) by the reduction of camphoroxalic acid, is equally compatible with either the keto- or hydroxy-formula.

Experimental.

Preparation of Ethylic Camphoroxalate, 



.—The various methods of preparation described below were tried in order to determine the most favorable conditions for the formation of this compound.

I. *Sodium Wire and Ether.*—Camphor (21 grams = $1\frac{1}{8}$ molecule) was mixed with ethylic oxalate (14.6 gram = 1 molecule), and ether (200 cc.) purified by means of sodium, and sodium (2.3 gram = 1 atom) in the form of thin wire quickly added. A white flocculent precipitate is soon formed; this turns yellow in a few moments, and then dissolves; the ether usually boils vigorously, but cooling is scarcely necessary. When the reaction slackens the flask, attached to a reflux-condenser, is heated on the water-bath during 10–15 minutes, and then allowed to remain at the ordinary temperature for about twenty-four hours. A small

quantity of the sodium salt usually remains undissolved. The ethereal solution is poured into ice-water, well shaken, and the ethereal layer removed. The aqueous solution is again extracted with ether, the latter being added to the first extract (Sol. *A*). More ether is added to the aqueous liquid, and then dilute ice-cold sulphuric acid in excess. After shaking, the ether is removed, and the residue extracted twice more with ether. The three ethereal solutions are combined, dried over calcium chloride, and distilled. The residue consists of crude ethylic camphoroxalate together with some ethylic oxalate. The aqueous residual liquid does not react with copper sulphate solution even in presence of ammonia. The ethereal solution *A* is dried, the ether removed, and the residue, consisting of camphor, borneol, and camphoroxalic acid is mixed with concentrated sodium hydrate solution in considerable excess, dilute alcohol being added so as to bring the whole into solution; the liquid is then boiled during 1–2 hours, the greater portion of the alcohol is distilled off, the residue mixed with water, filtered, and well washed. The whole of the borneol and camphor remain on the filter. The filtrate is treated with dilute sulphuric acid in excess, extracted three times with ether, and this, when dried and distilled, leaves the camphoroxalic acid, which, after crystallization once or twice from ligroïn of low boiling-point, is sufficiently pure for ordinary purposes. The yield of ester and purified acid is 58 per cent. of the theory.

II. *Sodium Wire and Ligroïn* (*Boiling-point 64-70°*).—The ligroïn is carefully dried over sodium wire. The experimental details are similar in every respect to the foregoing, but the borneol, etc., is removed by means of ligroïn, the extractions after acidification being made with ether. The materials were taken in the proportion given in the previous experiment except that 300 cc. ligroïn were employed. The yield of crude ethylic salt alone was 63.5 per cent. of the theoretical. The reaction appears to proceed somewhat more slowly than when ether is used, and the mixture requires heating for a rather longer period. Camphor (31.5 gram =

1.5 molecule), ethylic oxalate (21.9 gram = 1 molecule), sodium (3.5 gram = 1 atom), and ligroïn (500 cc.) gave a combined yield of ester and acid of 92.4 per cent. of the theoretical. Camphor (44.6 gram = 2 molecules), ethylic oxalate (21.8 gram = 1 molecule), sodium (6.9 gram = 2 atoms) and ligroïn (500 cc.) gave a combined yield of 66.5 per cent. of the theoretical. This experiment was made in order to test, as far as possible, whether the mechanism of the reaction accorded with the explanation given in the theoretical part, or whether the camphor and sodium first reacted according to the equation $2C_{10}H_{16}O + 2Na = C_{10}H_{18}ONa + C_{10}H_{17}ONa$. The sodium dissolved comparatively slowly, and the liquid required heating on the water-bath during about thirty-five minutes. The ethylic salt was darker than usual (see later).

III. *Sodium Ethylate and Ether.*—The sodium ethylate was made from Kahlbaum's absolute alcohol, dried in a current of purified hydrogen, powdered, and passed through a fine sieve. For the experiment it was suspended in ether that had been purified by means of sodium, the camphor and ethylic oxalate were added in equimolecular proportion, and, as no reaction occurred at the ordinary temperature, the mixture was boiled during eight hours with a reflux-apparatus. It gradually turned yellow, but the sodium salt did not dissolve to any great extent. The contents of the flask were poured into ice-water, acidified with dilute sulphuric acid, and worked up in the usual manner. The crude ethylic salt gave the ferric chloride reaction, but, when hydrolyzed in the manner described in the first paper, the yield of acid was only 10 per cent. of the theoretical. The method is therefore useless, as a means of preparation.

IV. *Sodium Ethylate in Alcoholic Solution.*—The sodium (1 atom) was dissolved in absolute alcohol in a reflux-apparatus, the camphor and ethylic oxalate added in equimolecular proportion, and the solution heated on the water-bath during 3–4 hours. Rather more than half of the alcohol was distilled off, the residue poured into ice-water, and treated as in the preceding experiment, except that the liquid was extracted

four times with ether. The crude ethylic salt deposited crystals of camphor after some time. It was converted into the acid of which it yielded 4.4 per cent. of the theoretical. Like the preceding method, this is quite unsuited for the preparation of the compound. The following table gives a comparison of the results obtained, methods III and IV being omitted for the reason stated :

Experiment.	Menstruum.	Molecules camphor to 1 molecule ethylic oxalate.		Atoms sodium.	Crude ethylic salt and acid. Per cent. of theoretical.
1	Ether	$1\frac{1}{3}$	:	1	58.0
2	Ligroïn	$1\frac{1}{3}$	:	1	63.5[1]
3	"	$1\frac{1}{2}$	:	1	92.4
4	"	2	:	2	66.5

As compared with ether ligroïn is beneficial to the yield: it has the advantages of cheapness and facility of dehydration, hence it was always employed for the preparation of the ethylic camphoroxalate on a large scale. The ethylic salt obtained in experiment III was comparatively pure, as shown by its behavior towards phenylhydrazine. The relatively small yield in experiment IV is discussed in connection with camphoroxalic acid.

In ethereal or ligroïn solution ethylic camphoroxalate does not react with an aqueous solution of copper acetate ; with neutral solutions it yields, on evaporation, a soft crystalline residue, which smells of camphor. An ammoniacal solution of copper acetate, under similar conditions, gives a green varnish. A further attempt to prepare a copper salt was made as follows : the crude ethereal solution of sodium ethylic camphoroxalate, containing therefore borneol, etc., was acidified with acetic acid and copper acetate added. No copper salt was precipitated, and none was obtained on evaporation. Ethylic camphoroxalate thus presents a marked contrast with formylcamphor, which is a strong acid. The influence of various radicles on the power of forming copper salts which 1,3-diketones exhibit, has been investigated to some extent by Claisen and Ehrhardt ;[2] ethylic camphoroxalate most closely approaches ethylic ethylacetoacetate in this respect.

An attempt was made to purify ethylic camphoroxalate by

[1] Ethylic salt only.

[2] Ber. d. chem. Ges., 22, 10.

distillation. After removal of traces of ether and alcohol, the temperature rose to 150°; the portion passing over at 180°–185° showed no definite boiling-point. A considerable carbonaceous residue was left in the flask, no sublimate (camphor) could be observed. The distillate gave the ferric chloride reaction. When again distilled (75 mm.) carbon dioxide was evolved at 103°; at 115° an oil passed over together with a crystalline substance, apparently camphor; it dissolved in the oil and, although separation took place at the temperature of a freezing-mixture, it redissolved too quickly to admit of removal. The distillate gave the ferric chloride reaction. From the residue in the flask, camphoroxalic acid was isolated in comparatively large amount. The distillate when further examined, proved to contain camphor, camphoroxalic acid, and an acid that rapidly reduced an ammoniacal solution of silver nitrate at the ordinary temperature. Oxalic acid could not be detected. The chief effect of heat on ethylic camphoroxalate is apparently to resolve it, no doubt by the agency of traces of water, which are unavoidably present, into alcohol and camphoroxalic acid, a little ethylic salt probably distils over; the remainder is then further decomposed into camphor and ethylic hydrogen oxalate which, at the temperature of the experiment, is resolved into carbon dioxide and ethylic formate. As the quantity of these substances was relatively small, it would appear as if the decomposition was chiefly confined to the ethylic salt. (Compare action of heat on camphoroxalic acid.)

It is known that ethylic malonate and ethylic oxalacetate can be separated from their alkyl derivatives by systematic treatment with solutions of sodium hydrate, sodium carbonate, and sodium hydrogen carbonate. The following experiments were therefore performed in the hope that in this manner the purification of ethylic camphoroxalate might be effected; at the same time the degree of its acidic properties, if any, would be exhibited. The ethylic salt was shaken with a solution of sodium hydrate (1 : 10) for a few moments, and the solution extracted with ether (Sol. *A*), which was then washed with dilute sulphuric acid. The aqueous residue was acidified with dilute sulphuric acid and extracted with ether

(Sol. *D*). This was washed successively with a solution of sodium carbonate (1 : 10) and a solution of sodium hydrogen carbonate (saturated). Both these solutions were then acidified and extracted with ether, giving solutions *B* and *C*, respectively. All the operations were performed as quickly as possible. The ethereal solutions, after being dried and the ether removed, gave residues as follows:

A. Greatest in amount; consisted chiefly of camphoroxalic acid.

B. Very small quantity of oil giving ferric chloride reaction.

C. One drop of colorless oil; no reaction with ferric chloride.

D. Two drops of slightly colored oil, giving ferric chloride reaction.

These results confirm the conclusions arrived at by a study of the behavior of ethylic camphoroxalate and copper acetate, and they show with what extreme readiness the ethylic salt is hydrolyzed; although possibly the pure compound might prove more stable in this respect.

Phenylhydrazine and Ethylic Camphoraxalate.

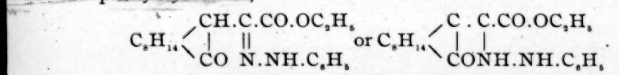
Ethylic camphoroxalate, in anhydrous ethereal solution, immediately reacts with phenylhydrazine (equimolecular proportions); the liquid becomes warm, and an oily solid is deposited; the mixture is boiled on the water-bath with a reflux-apparatus during four to five hours. The white, granular solid is separated by filtration, well washed with anhydrous ether, and recrystallized from a mixture of methylic alcohol and ether. It then appears homogeneous. When quickly heated it softens at 175°, and melts and evolves gas at 178°. Analyses showed that it is not quite pure. After recrystallization from the same solvent it is deposited in very slender, small, white needles, melting sharply at 212°. The yield is very good. Analysis gave the following results:

0.2043 gram substance gave 0.1374 gram H_2O, and 0.5220 gram CO_2.

0.1984 gram substance gave 13.8 cc. N_2 at 18.5° and 746.5 mm. = 744.1 mm. cor.

	Calculated for $C_{20}H_{28}N_2O_3$.	Found.
C	70.17	69.69
H	7.60	7.48
N	8.19	7.84

The compound is, therefore, the monophenylhydrazone or phenylhydrazide,



It was briefly described in the previous paper (loc. cit.) but, as the low melting-point (187°–188°) shows, it was not completely purified. The compound gives a deep blue purple coloration with concentrated nitric acid, is readily soluble in alcohol, less so in methyl alcohol, sparingly in ether, and in toluene. It is comparatively stable towards sodium hydrate at the ordinary temperature. When boiled, a faint pink coloration is produced. With ferric chloride and alcohol no color is obtained. The ethereal mother-liquor and washings collected during the preparation of the compound leave, on distillation, a red oil, which contains ethylic oxalate derived from the crude ethylic camphoroxalate employed.

Preparation of Ethylic Camphylphenylpyrazolcarboxylate.

This substance is formed by heating the phenylhydrazone just described at about 200°, steam being evolved, but its separation from unchanged hydrazone and oily products is attended with difficulty, and the yield is rather poor. It can also be obtained by warming the phenylhydrazone with acetic anhydride and fused sodium acetate. The product of the reaction is dissolved in water and on neutralizing with sodium carbonate the pyrazol is precipitated. It is formed when the phenylhydrazone is dissolved in glacial acetic acid, a few drops of concentrated hydrochloric acid added and the solution warmed on the water-bath during forty-five minutes. The acid liquid is diluted, neutralized with sodium carbonate, and the pyrazol extracted by means of ether. It is also obtained by saturating at 0° a solution of the phenylhydrazone in glacial acetic acid, with dry hydrogen chloride. The liquid is allowed to remain at this temperature during one and one-half hours, poured into water, and the solution

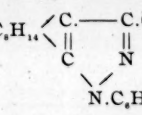
treated in the manner above described. The pyrazol is best prepared by suspending the finely divided phenylhydrazone, which need not have been recrystallized, in about half the quantity of absolute alcohol needed for its solution, and saturating the liquid at 0° with dry hydrogen chloride. The phenylhydrazone usually dissolves quickly, but occasionally a fugitive white flocculent precipitate is formed resembling aluminium hydroxide. The stream of gas is continued until a clear solution is obtained, and the liquid is then allowed to remain at 0° during one and one-half hours. The alcohol is distilled off on the water-bath, the residue washed with a solution of sodium carbonate, dried, and recrystallized from ether-ligroïn. The yield is practically quantitative. The compound crystallizes in bunches of white needles, melting at 114°. It is readily soluble in alcohol, less so in ether, and sparingly in ligroïn. It gives a pale yellow colored solution with concentrated nitric acid; is precipitated unchanged from its alcoholic solution by the addition of a solution of ferric chloride; is insoluble in a boiling solution of sodium hydrate, in boiling dilute sulphuric acid, but readily dissolves in hot acetic acid. The analysis gave the following results:

0.2758 gram substance gave 0.1847 gram H_2O and 0.7458 gram CO_2.

(1) 0.1557 gram substance gave 12 cc. N_2 at 18.5° and 744.5 mm. = 742 mm. (cor.).

(2) 0.2508 gram substance gave 19.2 cc. N_2 at 16° and 750.1 mm. = 748 mm. (cor.).

	Calculated for $C_{20}H_{24}N_2O_2$.		Found.
C	74.07		73.75
H	7.40		7.44
		(1)	(2)
N	8.64	8.66	8.78

The properties and mode of formation of the compound agree with the formula C_8H_{14}  .

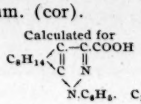
In the light of C. Walker's[1] investigation of the condensation-products of ethylic acetoacetate phenylhydrazide it is interesting to observe that ethylic camphoroxalate phenylhydrazone yields the same pyrazol both at high and at low temperatures.

Camphylphenylpyrazolcarboxylic Acid.

The preceding compound is readily hydrolyzed by dissolving it in the minimum quantity of alcohol, and adding potash (2 parts), dissolved in a little water. The solution is warmed on the water-bath during about thirty minutes until it becomes clear. It is then cooled, and acidified with dilute sulphuric acid. After remaining for a short time, the crystalline precipitate is removed, dried, and recrystallized twice from benzene, with or without the addition of ligroïn. The yield is quantitative. The crystals first formed consist of lustrous needles; they appear to contain some of the solvent as they slowly lose their lustre at the ordinary temperature, more quickly when warmed. The recently prepared crystals melt at 192°; after drying, at 197°. The acid is very sparingly soluble in water, and practically insoluble in ligroïn. It readily dissolves in benzene, and in hot toluene, but is less soluble in ether. Concentrated nitric acid gives no coloration; with alcohol and ferric chloride a brownish-red color is produced which becomes more red on heating. The compound has well marked acidic properties; it readily dissolves in a solution of sodium hydrate at the ordinary temperature, and in a solution of sodium carbonate on warming, carbon dioxide being liberated. From these solutions it is reprecipitated by acids. The analyses gave the following results:

0.3980 gram substance gave 29.2 cc. N_2 at 17.5° and 745.5 mm. = 743 mm. (cor).

0.2227 gram substance gave 19.6 cc. N_2 at 19° and 744 mm. = 741.5 mm. (cor).



	Calculated for $C_{18}H_{20}N_2O_2+\frac{1}{2}C_6H_6$.	Found. (1)	Found. (2)
N	9.45	8.35	8.30	9.86

[1] This JOURNAL, 14, 576.

The first analysis was made with air-dried material, the second with substance dried at 100°. The *salts* of the heavy metals are insoluble and amorphous. The copper salt is greenish-blue, the ferric salt buff, the lead and barium salts white.

Camphoroxalic Acid.

In the previous paper (*loc. cit.*) the preparation of this compound from ethylic camphoroxalate was described, but subsequent experiments have shown that its stability is much greater than was formerly believed to be the case, and that it is needless to hydrolyze at the ordinary temperature. Its separation from the crude borneol residues was also detailed. It is found that the use of sodium ethylate for this purpose is not necessary; sodium hydrate meets all requirements, as described above, in the preparation of the ethylic salt. An attempt was made to separate it from the borneol and camphor by distillation. The crude ligroïn-extract was dried, the ligroïn removed, and the residue fractionated; at 60°–100° a little ligroïn passed over, and the temperature then rose to 200°, at which point carbon dioxide was evolved, and a white sublimate formed. The contents of the flask did not boil at 220°. The sublimate melted at 192°–194°, and appeared to consist of camphor and borneol. The residue was freed from carbonaceous matter by sublimation, and melted at 180°–184°. It had a smell like that of camphor. The acid is insoluble in cold, but slightly soluble in hot, water. It crystallizes from ligroïn in hexagonal, not quadratic, plates, and the well-developed crystals resemble those of quartz in form. In a dilute solution of sodium hydrate it instantaneously decolorizes a solution of potassium permanganate. With lime water, or a solution of calcium chloride and ammonium hydrate, a white flocculent precipitate of the calcium salt is formed. This is readily soluble in acetic acid, and its production serves as a convenient test for the presence of the acid. The following table gives the yield of acid under varying conditions; the numbers of the experiments refer to the previous table (which see):

Experiment.	Ethylic oxalate—1 mol. Molecules camphor.		Atoms sodium.	Acid formed. Per cent. of theory.	Acid : 1 pt. of ester.
1	$1\frac{1}{3}$	:	1	4.9	0.07
3	$1\frac{1}{2}$	:	1	17.0	0.2
4	2	:	2	44.6	1.8

The production of the acid may be due to one or more of the following causes :

1. Traces of moisture in the apparatus employed. 2. Hydrolysis of the ethylic salt whilst the borneol is being extracted. 3. To the borneol and excess of camphor retaining ethylic salt which is afterwards hydrolyzed in subsequent operations (see above). 4. To hydrolysis by means of the sodium ethylate. No doubt some acid is produced by the first three causes, but as they were practically constant during all the experiments, they do not explain the gradual increase. As to the fourth possibility, whilst sodium ethylate readily hydrolyses fats and oils, there is no reason to suppose that it would act in this manner under the conditions mentioned. The proportion of acid formed is dependent apparently on that of camphor and sodium present, and, to some extent, on the duration of the heating. Its production appears to be analogous with that of acetophenoneoxalic acid described by Brömme and Claisen,[1] who explain the reaction by assuming the formation of the intermediate compound, $NaO.C(OC_2H_5)_2.C(OC_2H_5)_2.ONa$. In the case of camphoroxalic acid the additive compound would be either

$$NaO.C(OC_2H_5)_2.C\begin{cases}ONa\\OC_{10}H_{15}\end{cases} \quad \text{or} \quad \begin{matrix}NaO\\C_2H_5O\end{matrix}\!\!>\!C\!<\!\begin{matrix}ONa\\OC_2H_5\end{matrix}$$

according to whether the ethylic oxalate combines with two molecules of sodium camphor, or with one of this and one of sodium ethylate. The ortho compound then reacts with more camphor in the manner already described giving

$$C_8H_{14}\!<\!\begin{matrix}CO\\|\\C:CONa\end{matrix}.C\begin{cases}ONa\\OC_2H_5\\OR\end{cases}$$

which, when poured into water, yields

[1] Ber. d. chem. Ges., 21, 1132.

$$C_8H_{14}\begin{cases}CO\\ |\\ C{:}CONa\end{cases}.C\begin{cases}ONa\\ \diagdown O\end{cases} + C_2H_6O + ROH \ (R{=}C_2H_5 \text{ or } C_{10}H_{18}).$$

This explanation also accounts for the necessary prolongation of the heating.

Camphoroxalic Acid and Hydroxylamine.

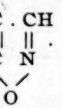
The acid (1 mol.) is dissolved in the smallest requisite amount of alcohol; an equal weight of hydroxylamine hydrochloride (3.5 mol.) is dissolved in the minimum quantity of water, the solutions mixed, more alcohol added, if necessary, then solid sodium hydrogen carbonate in excess. After remaining at the ordinary temperature during three to four days, the liquid, if sufficiently concentrated, becomes permeated with a mass of slender, colorless needles, consisting of a sodium salt. It is acidified with dilute sulphuric acid, extracted three times with ether, and the ethereal solution dried and distilled. The residue is purified by dissolving in ether, and adding ligroïn. It crystallizes in bushy clusters of colorless, lustrous needles, and in long narrow plates, and melts at 146.5° with evolution of gas. The yield is about equal to the weight of acid employed. The compound is readily soluble in water, methyl alcohol, and ether, almost insoluble in ligroïn and in dilute sulphuric acid. It is a comparatively strong acid and dissolves easily, at the ordinary temperature, in sodium carbonate, carbon dioxide being evolved, and also in a solution of sodium hydrate, and this, when boiled, does not evolve alkaline fumes. No coloration is produced with a solution of ferric chloride. Analysis shows that the substance is an additive compound.

0.2224 gram substance gave 0.1500 gram H_2O and 0.4554 gram CO_2.

0.1705 gram substance gave 8.6 cc. N_2 at 21° and 739 mm. = 736.3 mm. (cor.).

	Calculated for $C_8H_{14}\begin{cases}CH.C.OH(NH.OH)CO.OH\\ |\\ CO\end{cases}$	Found.
C	56.03	55.85
H	7.40	7.49
N	5.44	5.55

The copper and lead salts are apparently amorphous; the former is pale blue, the latter white; both are formed only in ammoniacal solution.

Camphylisoxazole, C_8H_{14} 

The preceding compound (1 part) is dissolved in a mixture, consisting of glacial acetic acid (2 parts) and acetic anhydride (1 part), and the solution heated for a few minutes on the water-bath until the color darkens. It is then poured into water, neutralized with sodium carbonate, and extracted three times with ether. The ethereal solution is dried, the ether distilled, and the residue purified by solution in glacial acetic acid. On the addition of water, colorless lustrous needles are formed, melting at 124°–125°. The compound slowly sublimes at about 70° and is deposited in clusters of very slender, silky, lustrous needles. It is readily soluble in glacial acetic acid, ether, toluene, and alcohol; almost insoluble in ligroïn. It instantly dissolves in concentrated nitric acid, but gives no coloration with it or with ferric chloride and alcohol. It dissolves in water, and in a solution of sodium carbonate when boiled, and in a solution of sodium hydrate on warming, but is reprecipitated from all three by cooling. The analyses gave the following results:

(1) 0.2257 gram substance gave 0.1697 gram H_2O and 0.6122 gram CO_2.

(2) 0.2238 gram substance gave 0.1693 gram H_2O and 0.6058 gram CO_2.

0.1637 gram substance gave 11.4 cc. N_2 at 16° and 745.1 mm. = 743 mm. (cor.).

	Calculated for $C_{11}H_{18}NO$.	Found. (1)	(2)
C	74.57	73.97	73.82
H	8.47	8.35	8.40
N	7.91	7.93	....

I should like to take this opportunity of expressing my thanks and obligations to Prof. Edgar F. Smith for his kindness in allowing this work to be continued in the John Harrison Laboratory.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA.

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE PREPARATION OF ZINC ETHYL.

By Arthur Lachman.

Of all the methods heretofore proposed for the preparation of zinc alkyls, the Gladstone-Tribe copper-zinc couple[1] gives by far the best results. As originally given, however, the directions are open to two practical objections. First of all, it is not always an easy matter to secure the zinc filings of necessary fineness. And secondly, while the careful fusion of the filings with the reduced copper offers no difficulties when carried out with 10-gram lots, as usually taken by the authors, it is practically impossible to prevent larger quantities from melting completely and forming a worthless solid ingot on cooling.

A form of zinc available in every laboratory is zinc dust. On removing the coating of oxide by heating in hydrogen for a short while, it was found that 50 grams each of the metal and ethyl iodide reacted within ninety minutes, and gave 14 grams of zinc ethyl (72 per cent. of the theoretical yield). When this metal is coupled with copper, by reducing an intimate mixture of zinc dust and finely powdered copper oxide, the time of reaction is shortened to thirty minutes, and the yield increased to nearly 90 per cent. Different varieties of zinc dust give different yields (ranging from 70 per cent. upward); this probably finds its explanation in the phenomena discussed by H. Wislicenus.[2] The actual quantities of materials taken also exercise an influence, the yield being somewhat smaller with larger quantities (100 grams or more). I have not attempted to ascertain the cause of this.

The details of the process are extremely simple. Zinc dust and copper oxide are mixed in the ratio of 100 to 12, loosely filled into a combustion-tube, and a current of hydrogen passed over the heated mixture for about twenty minutes. In order to prevent the condensation of moisture in the tube, with the consequent caking of the mass, it is best to heat the tube along its whole length at once. A dull red heat seems to give the best results; the nearer the melting-point of zinc

[1] J. Chem. Soc., 1879, 570. [2] J. prakt. Chem. (2), 54, 18 ff.

the better, I presume. If the temperature be kept too low, the metals do not alloy well, and the results approach those given by zinc dust alone. I have usually employed equal quantities of ethyl iodide and metal couple, sometimes less metal; perhaps the yield might be increased by excess thereof. For further directions the article of Gladstone and Tribe had best be consulted. In place of the oil-bath for heating the zinc ethiodide, the Babo air-baths may be substituted, as being cleaner and more expeditious; if a small flame be placed under them at first, there is no danger of breaking the flask. By employing two sets of apparatus, and working up about 100 grams at a time, the process may easily be made continuous, and several hundred grams of zinc ethyl prepared in a single day. Mr. F. M. Tschirner, who has manufactured nearly 300 grams for me, found no difficulty in obtaining 150 grams in an afternoon.

It is customary to preserve zinc ethyl in sealed tubes. This is awkward where small and varying quantities are frequently needed. Small Erlenmeyer flasks, with perfectly straight sides beginning at the very mouth, greatly facilitate the operation of pouring out the liquid, and when well corked form perfectly safe receptacles. Instead of requiring an assistant to keep a stream of carbon dioxide upon the mouth of the flask when transferring zinc ethyl, it is much more convenient to conduct all such manipulations under a small, inverted funnel, through which the gas is rapidly passing.

It had been my intention to compare the above described modification of the copper-zinc couple with the original, chiefly with respect to its reducing powers, but the recent article of H. Wislicenus[1] has made this unnecessary. Qualitive tests show that the new form reacts in much the same manner with alkyl and alkylene haloids as the older. I have attempted to use ethyl bromide in place of the expensive iodide, but without encouraging results. Methyl iodide reacts as readily as the ethyl compound, though the yield of zinc methyl was not determined.

ANN ARBOR, Dec., 1896.

[1] *Loc. cit.*

A SIMPLE TEST FOR THE HALOGENS IN ORGANIC HALIDES.

By J. H. Kastle and W. A. Beatty.

In connection with some work on the displacement of bromine and iodine from their organic compounds, we had frequent occasion to test for the halogens in their organic derivatives, and, while a great many methods for conducting such tests were to be found in the literature, few, if any of these, could be conducted rapidly; and many involved the use of rather large amounts of substances, such as lime, soda-lime, etc., which are not readily obtained free from chlorine. It is unnecessary in this connection to enumerate the many tests which have been proposed for these elements in their organic compounds; most of them are already familiar to chemists, and nearly all of them are described in Beilstein's *Handbuch* and in Allen's *Commercial Organic Analysis*.

Appreciating the need therefore of a simpler and rapid test whereby chlorine, bromine and iodine could be recognized with certainty in their most stable and volatile organic combinations, it occurred to one of us (Kastle) to heat such compounds with a mixture of silver and copper nitrates, thereby oxidizing the organic matter and holding back any halogen present by means of silver. On experiment it was found that excellent results could be obtained with this mixture, which can always be obtained free from any traces of chlorine, bromine or iodine, by dissolving the metals in pure nitric acid and evaporating to crystallization. In the case of non-volatile substances the test is most easily conducted as follows: A small quantity of a substance to be tested, usually about 0.1 gram, is placed in the test-tube, along with about 0.5 gram of the mixed nitrates and a few drops of water. The tube is then gradually heated in the flame of the Bunsen burner until the nitrates are completely decomposed; the temperature never being allowed to rise higher than low red heat. The tube, in which some reduced copper is often seen, is allowed to cool, a little water and dilute sulphuric acid poured on the contents of the tube and a few pieces of metallic zinc added. After five or ten minutes, during which time any halogen compound of silver is reduced, the contents of the tube are filtered

and a solution of silver nitrate added to the filtrate, together with a little dilute nitric acid, when the chloride, bromide or iodide of silver will be precititated, if either of these halogens was present in the substance tested.

Excellent tests for chlorine, bromine and iodine were obtained in this way in the following substances: Dibromnaphthalene, eosine, benzene dichlorsulphonamide, *p*-brombenzenesulphonamide, tribromphenol, potassium *p*-brombenzenesulphonate, monobromacetanilide, sozoiodol (Merck), barium *p*-iodobenzenesulphonate. With very volatile substances such as chloroform, it was found necessary to conduct the test in a tube about six inches long by one-quarter inch internal diameter, closed at one end, and bent twice at right angles at equal distances along the tube, so as to form a tube having somewhat the shape of the letter S. In making the test about ¼ cc. of the volatile compound to be tested was introduced into the closed end of the tube, and the tube so clamped as to give its open end an upward slant. About 0.5 gram of the dry mixed nitrates was then placed in the bend of the tube farthest removed from the closed end; after which the parts of the tube containing the substance to be tested and the nitrates were heated alternately, the former portion very gently, so as not to drive out the volatile substance before it could be oxidized by the decomposing nitrates. The heating is continued until all the nitrates are decomposed, and all of the substance to be treated volatilized, at the end of which time the tube is broken and the fragments, containing the oxides of copper and silver, placed in a test-tube with a small quantity of water and sulphuric acid and a few small pieces of zinc. The test is then completed in the manner described in the above. The following substances were tested in the closed S-shaped tubes with excellent results in every case:

Chloroform, isopropyl bromide, butyl bromide, ethyl chlorcarbonate, propyl bromide, propyl iodide, bromoform, ethylidene chloride, propyl chloride, monobrombenzene, dibrombenzene, ethylene bromide, monochloracetic acid, benzoyl chloride, dibromsuccinic acid.

It is believed that this test as applied both to volatile and to non-volatile organic halides has in it many points of advan-

tage over those which have been proposed for this purpose; in the first place the test is rapid and certain in its result, and by means of it we can judge not only of the presence or absence of the halogens, but it can also be determined at a glance whether it is chlorine, bromine or iodine that is present in the organic compound. Secondly, only very small quantities of substances are required to make the tests, and the few simple reagents needed may be obtained free from any traces of halogen without the least difficulty.

STATE COLLEGE OF KENTUCKY,
FEBRUARY, 1897.

REVIEWS.

COMMERCIAL ORGANIC ANALYSIS: A treatise on the properties, proximate analytical examination, and modes of assaying the various organic chemicals and products employed in the arts, manufactures, medicine, etc.; with concise methods for the detection and determination of their impurities, adulterations, and products of decomposition. By ALFRED H. ALLEN, F.I.C., F.C.S. Second Edition. Revised and enlarged. Vol. III. Part III. Philadelphia: P. Blakiston, Son & Co. 1896.

In the preface to the last previously issued portion of this valuable work (in 1892), it was announced that Part III of Volume III would cover the whole of the then remaining ground, and complete the work. But the author has decided to reserve the subject of Proteids and Albuminoid Compounds for still another part, and has included in that recently published the alkaloids not already disposed of, the glucosides, unclassified vegetable bitter principles, the animal bases and acids, and cyanogen with its derivatives. These subjects are treated with the same care, clearness and comprehensiveness which have given character to the earlier portions of the work.

There is much of interest for the physiological chemist and medical man, and the chapter on the ptomaines is valuable from a medico-legal point of view, while the recent great extension in the use of the cyanide process for the extraction of gold gives commercial importance to the discussion of cyanide liquors, the assay of residues from electroplating and gilding, and from gold extraction, etc.

It is particularly satisfactory to find, along with careful consideration given to the work of others, so much evidence of individual laboratory experience on the part of the author himself. Mr. Allen's book deserves its well established place as one of the standard classics of the working chemical library.

J. W. MALLET.

ENGINEERING CHEMISTRY: A Manual of Quantitative Chemical Analysis, for the Use of Students, Chemists and Engineers. By THOMAS B. STILLMAN, M.Sc., PH.D., Professor of Analytical Chemistry in the Stevens Institute of Technology. Easton, Pa.: Chemical Publishing Co. 1897.

It is not very easy fairly to judge this work. Its scope and intention are not clearly indicated by its title or by its table of contents. It is certainly not a general manual of quantitative chemical analysis; yet it begins with some exercises evidently intended for elementary study in this field, such as the "determination of sulphur trioxide in crystallized magnesium sulphate," and the "determination of chromium trioxide in potassium bichromate." On the other hand, if it be taken as a special treatise on chemical analysis applied to the purposes of the engineer, one sees with some surprise in the body of the work a discussion of the "determination of sulphuric acid and free sulphur trioxide in fuming Nordhausen oil of vitriol," (introduced immediately after the "determination of aluminum in iron and steel," and immediately before the "determination of manganese in iron and steel"); and of "sodium cyanide as a component of potassium cyanide," (just before the "chemical and physical examination of Portland cement"); chapters on "the chemical and physical examination of paper," and on "soap analysis,"—subjects but distantly related to engineering—and on "practical photometry" and "the electrical units," which are not chemical subjects at all.

While some of these matters appear rather out of place, there are others which, it would seem, might well have been included, but are not, as, for instance, the examination of ordinary lime and lime mortar, of stucco (plaster of Paris), and of explosive agents.

A good many small errors, and an occasional careless use of language, strike the eye of the reader, and produce an uneasy feeling that there may possibly be other and more serious defects of this kind amid the numerous facts and figures in the five hundred pages of the book. For example, on page 58, "Charlestown, S. C.;" on page 81, "Glosway" (for Ilosway or Ilosvay); at same place, "a solution of α-amidonaphthalene acetate," it is directed, is to be made thus, "two-tenths gram of naphthylamine is boiled with forty cc. of water," (no mention of acetic acid, which is moreover especially recommended by Ilosvay), "filtered and diluted to 400 cc." It would have been well to note that the solution he has recommended will not keep unaltered. On page 94 we note "The middle portion of the scale" (boiler scale) "was a mixture of carbon dioxide and the hydrated oxides"; on page 303,

"Saara*n*" (for Saara*u*); on page 319, "Guthrie's" ("Gutrie's" in table of contents), "e*n*tectic" (for e*u*tectic) "alloys"; and on page 488, in the table of atomic weights of the principal elements, oxygen being taken = 16, the values given for the following elements are, "aluminum 27.5," "antimony 120.0," "barium 137.0," "tin 118.0," "uranium 240.0," "wolfram (tungsten) 184.0," and "zinc 65.0."

In connection with the methods for determining the individual constituents of substances examined, the *reasons* for making such determinations, and the practical use to be made of the results, are given in an irregular way, and with very different degrees of fulness and clearness.

There is undoubtedly much valuable matter in the book, but it cannot be said that it is well arranged, or digested with the precision and clear perspective in the exposition of general principles and minute details that makes a work of standard and permanent value. J. W. MALLET.

PTOMAÏNS, LEUCOMAÏNS, TOXINS AND ANTITOXINS. BY VICTOR C. VAUGHAN, PH.D., M.D., AND FREDERICK G. NOVY, SC.D., M. D. Third edition, revised and enlarged. Lea Brothers & Co. pp. 604.

The investigation of the chemical factors involved in disease, and the study of the chemistry of bacteria and cells in general, have received increased attention during recent years. The results thus far obtained have been incomplete and unsatisfactory in many ways, and it has been a difficult task to compile and classify the data at hand. The third edition of Vaughan and Novy's Ptomaïns and Leucomaïns is a worthy successor to the two that have preceded it. The new volume has been carefully revised, and over 200 pages been added to the former contents. Among the material presented for the first time is a brief chapter on the examination of poisonous foods; the germicidal constituents of the blood are discussed with particular reference to recent work on the nucleins, and the problems of immunity and serum-therapy are treated in the light of the newer investigations. Referring to the more purely chemical portions of the book, practically all the important contributions of the last six years have been included. Thus, new material has been added to the description of muscarin and the members of the cholin group (p. 383). In the chapter on the chemistry of the leucomaïns the discussion of the basic constituents of the cell has been adapted to the results of the recent investigations of Kossel, E. Fischer, Drechsel, Krüger, Balke, etc. In this connection the detailed description of the chief methods for the separation of the alloxuric bodies (p. 475 ff.) is a valuable

feature, as well as the consideration of the constitution of these compounds (p. 481). The work of Vaughan and Novy cannot fail to create a favorable impression; the treatment of the subject matter, though mainly historical, shows no lack of critical features (cf. p. 321), while new problems are suggested at every step. In a few instances there is revealed an obvious lack of proportions, as for example, in the chapter on foods containing poisons—of the entire eighty-one pages, no less than twenty-four are devoted to tyrotoxicon, a ptomain of undetermined composition isolated by Vaughan from poisonous cheese. The newer scientific nomenclature has been adopted for the most part, and the terms chemic, physiologic, chlorid, etc., replace the more familiar spelling. There are remarkably few errors, typographical or other. On p. 384, the structural formula for cholin is incorrectly printed. A complete and well arranged bibliography concludes a volume that forms a welcome and thoroughly valuable addition to current physiologico-chemical literature.

LAFAYETTE B. WENDEL.

A LABORATORY MANUAL OF INORGANIC CHEMISTRY. By RUFUS P. WILLIAMS. In charge of the Chemical Department of the English High School, Boston, etc. Boston: Ginn & Co. 1896.

This little book gives quite minute directions for the performance of one hundred experiments or laboratory exercises. It is intended to accompany some text-book and is evidently provided for a rather young set of pupils, the desire apparently being to have all the members of the class engaged at the same work at one time. This may frequently be necessary on account of a too small teaching staff, or for the convenience of the instructor; it is as frequently a disadvantage to the pupil. For if one thing seems evident in laboratory instruction, it is that the time required by different students for the performance of the same task is rarely the same. With the adoption of the drill system of experimentation the opportunity for the development of anything but a perfunctory method of work, would seem to be shut out.

It is hard to decide by a study of the experiments alone what the pupil will learn from their performance in connection with the study of a text-book. In response apparently to a demand which seems as wide-spread as it is inexplicable, the author plunges the student with far too little preparation into the labyrinth of qualitative analysis and "separations."

While the book by no means merits praise as if it were an ideal laboratory guide, it must be said it is quite full in its description of individual experiments and clear: of its kind it seems to be good—a kind, however, which too often teaches,

"The science of chemistry consists in the memorizing of formulas and the balancing of equations." W. W. R.

LABORATORY CALCULATIONS AND SPECIFIC GRAVITY TABLES. By JOHN S. ADRIANCE, A.M. Third edition, revised and enlarged. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1897. 144 pp. Price, $1.25.

This book is interleaved with blank pages and contains a collection of tables from various sources, including those for comparison of different systems of weights and measures, preparation of reagents, specific gravity and composition of a number of solutions, calculations of analytical results, and other odds and ends. The author states in the preface that his aim has been to offer to the student, as well as to the analytical chemist, a substitute for much of his laborious calculations. The arrangement in some of the tables is not systematic and no explanations are given as to their use, so that one who has had no previous experience in the use of such tables would perhaps find difficulty in interpreting them. In the tables for the conversion of $BaSO_4$ to S, $Mg_2P_2O_7$ to P_2O_5, and P_2, and some others, the calculations are made only to the second decimal, so that differences of less than ten milligrams cannot be determined by their use. As all determinations are accurate at least to the milligram, the additional calculations would have to be made and while the tables were being examined and the extra calculation made, the whole could be determined by use of the factor or by other simple methods. Although the book contains some tables which are of use in special cases, it cannot be recommended as suitable for general use, as intended by the author. J. E. G.